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Mechanisms of Deterioration of Nutrients

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1. General Introduction

Phase III of this contract has been devoted to continuation of studies to develop methods by which freeze dried foods of improved quality will be produced. Studies of storage stability of freeze dried fruits were initiated. Development of artificial food matrices as a high quality item for incorporation into various products is progressing on schedule.

In particular, studies have continued in the following areas, each of which is covered in a separate section of this report.

Section 2: Microscopic Investigations of Freeze Dried Systems

Studies on the formation of structure and separation of phases during freezing and freeze drying of emulsions has been investigated for several model systems. These studies have utilized the freeze drying stage for the optical microscope, and have involved the development of a number of microscopic techniques for use with the optical and scanning electron microscopes. This work will provide a basis for development of emulsion-based freeze dried foods.

Section 3: Browning of Dried Foods at High Temperatures

Deterioration of organoleptic quality of freeze dried foods due to high temperature heating has been studied. Comparisons have been made between heating during or after freeze drying. The relative effects of heating temperature on quality loss due to browning and rate of product throughput has also been evaluated.

Section 4: Artificial Food Matrices (AFM)

A two-step gelation procedure has been developed which permits rapid fabrication of artificial food matrices whose texture simulates fruit. The artificial food matrices may be flavored as desired. These matrices may be frozen and thawed or freeze dried and rehydrated without loss of the desirable texture.

Section 5: Freeze Dried Food Products of Improved Quality

A wide variety of freeze dried fruits of high quality have been prepared using the results obtained in the various areas of this contract. The influence of additional process variables and methods have been evaluated. Tests on the influence of temperature and moisture content on stability during storage has been initiated.

A Summary of the results of Phase III is presented as Section 6.

In accordance with the Phase III end item, 5 lbs. of a freeze dried product incorporating the artificial food matrices will be sent to NASA/JSC.

2. Microscopic Investigation of Freeze-dried Systems

2.1 Introduction

Structure of freeze-dried oil-in-water emulsions was studied. The systems contain organic non-volatile solutes which serve as the matrix of the freeze-dried material.

To describe the location of the lipid phase in freeze-dried emulsions, a variety of microscopic analytical methods have been applied. These methods include the use of a freeze-drying stage for the optical microscope, use of lipid soluble stains, use of polarising techniques to detect anisotropy, use of gold coating of dried samples to improve observational detail in the optical microscope and use of the backscatter mode in the scanning electron microscope. Autoradiographic techniques with C^{14}-labelled oil phase components were used in some exploratory tests.

2.2 Description of Microscopic Techniques

2.2.1 Freeze-drying microscope stage

The design of the freeze-drying microscope stage which was described previously (Phase I Annual Report) was modified to allow very rapid cooling (250°C/minute). This is achieved by cooling nitrogen gas in a liquid nitrogen heat exchanger and using this gas to cool the sample by direct contact. A freeze-drying stage of this new design was constructed.

Temperatures are measured by insertion of a stainless steel-sheathed microthermocouple into the samples. The temperature controller regulates a solenoid valve so that the nitrogen gas either flows through the chamber or is vented, allowing the temperature in the sample to be controlled. To initiate freeze-drying, the flow of nitrogen gas into the chamber is stopped and the exit sealed. Refrigerated nitrogen is allowed to flow through an internal path in the stage which permits temperature maintenance during freeze-drying.

Dried compressed air is gently blown across the upper and lower windows of the stage to prevent condensation of environmental water vapor.

2.2.2 Staining of Lipid Phase

To improve oil droplet contrast, the oil phase was stained with a fat soluble dye, Sudan Black B. While the contrast between the oil and the dry solid phase is improved,

so that many fat droplets can be clearly distinguished, staining did not significantly improve sharpness of the oil droplets in frozen samples. It was also noted that the dark color of the oil inclusions due to staining could lead to confusion of these oil droplets with air inclusions in dried systems.

Observational clarity has been greatly improved by means of incorporation of another lipid soluble dye ("Fett Rot," or Fat Red 7B of Sigma Chemical Co.) The dye is first dissolved in a minimal volume of hexanol, and then mixed with the lipid prior to forming the emulsion. The lipid droplets, in both the liquid emulsion and in the freeze-dried material, have a distinct red color, providing visual color contrast and improved contrast when photographir with black/white film. Use of a blue daylight filter in the optical system gives additional color contrast, while incorporation of the standard green photographic filter somewhat reduces the effect. It has also been shown that the dye causes no differences in the structure of the resulting freeze-dried material. However, the dye did not allow visualization of any surface deposits of oil. This could be due to the very thin layer of these deposits so that the dye content is not sufficient to exhibit visual color contrast.

A method to visualize surface fat deposits has been investigated. It is based on the reaction of osmic acid

(OsO_4) with unsaturated bonds in oils, e.g. triolein and linoleic acid. Free fat deposits on the surface of a freeze-dried emulsion would thus be rendered visible, macroscopically as well as microscopically.

Osmic acid is sublimated directly onto the fat-containing sample by the following procedure. All steps are conducted in a chemical fumehood as osmic acid vapors can be harmful. The freeze-dried powder is placed on a slide inside a desiccator and a sealed ampoule containing a few crystals of osmic acid is broken and placed next to the sample. The desiccator is closed and the reaction proceeds as the vapor space equilibrates with osmic acid vapors with free fat turning dark due to reaction with the osmic acid vapors. The degree of darkening, which can be easily observed with the naked eye, varies from light brown to black depending on exposure time (10 minutes to 45 minutes) and the oil used (linoleic acid reacts faster than triolein).

In the optical microscope, the individual grains contain easily recognizable darkened areas where surface oil is present. Inclusions of fat do not react with the osmic acid, due to the impermeable carbohydrate matrix. The matrix solids themselves (e.g. maltodextrin and urea) do not react with the osmic acid, so this method is very specific for identifying surface deposits and free globules of fat.

2.2.3 Procedures Based on Refractive Index

Contrast in a microscopic sample is dependent in part on differences in refractive indices of the components. For this reason, model systems based on 1-bromonaphthalene as the oil phase are successfully used, since its high refractive index of 1.656 (for comparison water is 1.33, maltodextrin is 1.5, and triolein is 1.456) relative to the aqueous phase and the solid support results in a high visual contrast and sharpness of the droplets.

Since triolein is polymorphic and some percentage of the oil will be in the solid state at low temperatures, birefringence is exhibited. The fat has, however, a low degree of birefringence and oil inclusions appear as regions of 1st order grey interference color when viewed with crossed polarizers in the optical microscope. Improved contrast is obtained by insertion of a quarter wavelength quartz plate in the microscope's light path, resulting in the appearance of higher order interference colors (red, blue, yellow). The method is only useful for dry amorphous systems. In crystalline systems and in frozen systems, the birefringence from the solute crystals and ice dominates, and any effect due to the triolein is lost.

2.2.4 Gold Coating Samples for Optical Microscopy

To improve the clarity of a dried emulsion in the optical microscope samples were attached to a glass slide

with the help of double sided adhesive tape, and the slide and sample coated with a thin layer of gold at a 45 degree angle by vapor deposition under high vacuum. It was found that a sample coated with gold in this way exhibits very good contrast; i.e. when viewed in green light the contrast between the polysaccharide grain itself, oil inclusions, and holes and cavities is greatly improved due to appearance of various shades of green, brown, and black. It was observed that oil inclusions are black to dark brown due to the absorbance of light; broken shells and bumps are light brown indicating that they are empty (i.e. lost lipid or air), oil inclusions appear jet black, the carbohydrate appears green and holes are as light as the background field of view (Figure 1). This method allows detailed optical microscopy, using the same preparations as needed for scanning electron micrographs permitting direct comparisons. Placement of the sample in immersion oil improves sharpness but is not a necessary step. Coating the sample with an additional gold layer at a different angle can also improve the observational clarity.

2.2.5 Mapping of samples

Sequential studies with optical and scanning electron microscopes are used in evaluating sample structure. It is necessary to have a way of mapping the samples so that the same location can be observed in both instruments. In concept a sample is first scanned in the optical microscope

while in the dry state. The sample is gold coated and viewed in the scanning electron microscope. The gold coated sample is then transferred back to the optical microscope and viewed in the dry state or in immersion oil for more detailed study.

To locate particular areas in a single grain or in a sample prepared using the microscope freeze-drying stage, the following procedure is utilized: Individual grains are attached with double stick tape to a glass slide which has been etched with a grid. The structure and overall contour of the grains can be determined by viewing through a low power stereo microscope and recorded as a hand drawing or photograph. The slide is first viewed in the optical microscope and then the slide (with sample) is attached to a SEM stub, gold coated and viewed in the scanning electron microscope. Following SEM examination, the slide with gold-coated sample is detached from the SEM specimen stub and used for further examination in the optical microscope.

In this way it has been possible to compare the exact same areas in a specimen by both optical and scanning electron microscopy.

Figure 2 demonstrates the usefulness of being able to view the same sample by both optical and scanning electron microscopy. (Due to differences in angle of tilt in each instrument, the views are not precisely superimposable.) In figure 2a the SEM mode shows the overall surface morphology of a freeze-dried emulsion of 1-bromonaphthalene

(10%), emulsifiers (1% Tween 80 and Tween mos-100vs), maltodextrin (20%), and water. The area on the right hand side shows an apparently very smooth surface, on which a few details are distinguished: holes (a, a'), an elongated bump (b), an area of bumps (c), a ridge (d), and a wall (e).

Figure 2b is the optical microscopic view of the same field. The maltodextrin wall (e) now appears as a black shadow, and the ridge (d) appears as a thin white line. The holes (a) appear as bright white spots and are easily recognized. The elongated bump (b) shows up as a black area and is positively identifiable as an air inclusion (which is impossible with the SEM). The bumps (c) are only partially visible, but appear to be 1-bromonaphthalene. It should be noted that the dark grey area adjacent to the big hole (a') has been identified as a Tween 80 inclusion, and this is not at all visible in the SEM picture. The most striking difference between the two photographs is the 1-bromonaphthalene inclusions, which are observable in the optical micrograph as dots; while the electron micrograph shows nothing but a smooth surface. This results in the conclusion that 1-bromonaphthalene is fully encapsulated in the maltodextrin.

2.2.6 Backscatter Mode in the Scanning Electron Microscope

The image produced in the scanning electron microscope is formed from secondary and reflected electrons which result

when the electron beam hits the sample. Secondary electrons are those emitted from the specimen with energies under 50 ev. Electrons with greater energies are regarded as backscattered (or reflected) electrons. By electronically eliminating the secondary electrons (coming mostly from low molecular elements such as C, H, and O) an image is formed primarily from electrons arising from higher molecular weight materials. By incorporating organometallic compounds (containing Fe, Pb, or Ag) in the lipid phase, a useful contrast should be developed in the dried emulsions. This contrast can be limited by the background "noise" induced by the coating material used, e.g. coating with gold gives higher background "noise" than if carbon is used.

The initial study which was conducted on a silver-containing autoradiography sample was inconclusive. It was felt that the thin gold coating (200-500A) prevented differentiation of the silver grains.

A coating of aluminum was tried since in earlier work it was noted that samples could be coated with an aluminum film and successfully observed in the SEM. Aluminum, with its much lower atomic weight should not shield the heavier elements and therefore new studies using aluminum coatings were conducted. A system of 1-bromonaphthalene (10%) and maltodextrin (20%) coated with aluminum was investigated. It was expected that the bromine could be selectively imaged in the backscatter mode.

A distinct difference was observed between the SEM and the backscatter mode. In the latter a very clear contrast was observed in the sample with dark areas intermingling with bright areas. It was not conclusively determined if the bright areas were produced by bromine in oil rich regions since they did not appear as isolated spots but rather as continuous layers. The dark areas, which were observed as dark isolated spots, seem to correspond to folds and depressions on the surface (i.e. resulting from surface topology). The possibility exists that the continuous bright regions are caused by surface layers of non-encapsulated 1-bromonaphthalene, though it could also be due to either high subsurface concentrations of 1-bromonaphthalene, or perhaps inadequate resolution in the SEM in backscatter mode.

The method of backscatter electron microscopy appears promising and studies using systems containing ferrocene (Fe) in the lipid phase will be conducted.

2.2.7 Autoradiography

Autoradiography was attempted as a means for locating oil inclusions present below the surface of the dried matrix. In this method, a radioactively labelled lipid phase is incorporated into the freeze-dried matrix. The dried samples are coated with a sensitive photographic emulsion and the samples are stored in complete darkness . β radiation from the lipid causes, upon development, the precipitation of metallic silver. Each location of silver grains is

indicative of a source of radioactivity and hence lipid. The silver appears as black grains in the optical microscope, and in this way can be indicative of lipid in the sample.

Initial studies, using dried maltodextrin grains containing ^{14}C-propanol were generally unsuccessful because coating with the liquid photo emulsion resulted in partial dissolution of the samples. Those parts of the sample which remained undissolved showed encouraging results.

Autoradiography emulsion is also available in a film form (known as "stripping film") which is floated on water. The sample is quickly dipped under the film and raised up carrying the film off the surface. Due to the short duration of contact of the sample and water, less dissolution of the sample resulted, but still the results obtained were not of the desired usefulness and quality.

Further attempts to prevent dissolution of the sample have centered on protecting the sample surface by formation of a thin water-impermeable layer prior to treatment with the photographic emulsion. A number of non-polar liquids have been utilized as an initial dip, with some such as carbon tetrachloride giving partial success. It was noted during these studies that extended contact of the freeze-dried material and the non-polar liquid is possible with no change in structure of the freeze-dried sample. The most recent experiments into protection of the freeze-dried material has involved the deposition under vacuum from the vapor state of a thin coating of wax. When maltodextrin

grains which were mounted on a slide and then wax coated were dipped into water, no dissolution of the maltodextrin was observed. Further evaluation is required to determine the response of a wax coated system to the autoradiography procedures.

2.2.8 Fat Extraction Experiments

Since presence of oil could not be verified during scanning electron microscopy of oil-avicel freeze-dried emulsions, and to a certain extent on oil-maltodextrin systems, it was considered that oil might be lost during exposure of the sample to high vacuum in the gold evaporator (2×10^{-5} Torr) and in the SEM column (10^{-4} Torr). The heat of condensation of the gold could also be responsible for the apparent oil evaporation.

Rehydration of dried oil-avicel and oil-maltodextrin emulsions that had been subjected to gold coating and high vacuum showed qualitatively that oil globules were released from these systems and that the oil could be isolated by extraction with organic solvent.

Fat determinations were made on two emulsified systems

a) triolein - maltodextrin

b) triolein - avicel

to yield quantitative estimations of the amount of the possible oil loss.

The emulsions were prepared by mixing the solid in water (avicel is homogenized for 10 minutes to shred the

crystals to smaller pieces), adding the oil and homogenizing the mixture for 10 minutes. Aliquoits of 10 ml were frozen in liquid nitrogen, and freeze-dried.

Measurements of oil content were done in quadruplicates. Oil determinations were conducted on freshly made emulsion, freeze-dried emulsion, and freeze-dried emulsion subjected to high vacuum and gold coating in the evaporator (about 45 minutes at 2×10^{-5} Torr). The dried matrix is added to 10 ml water, stirred, and then 10 ml of chloroform are added. (The fresh emulsion is added to the solvent directly.) After transferring to a separatory funnel, the mixture is shaken for about 15 seconds. The phases are allowed to separate and the organic phase containing the extracted oil is isolated. The addition of chloroform is repeated twice and the three fractions are collected and the solvent is evaporated under vacuum. The remaining oil is then weighed.

The following results were obtained:

(Sample as mixed - Triolein 0.83g/Maltodextrin 1.0 g per 10 ml)

	oil content*	% of original oil
Fresh emulsion	0.59 g	71
Freeze-dried	0.60 g	72
After gold coating	0.61 g	73

(Sample as mixed - Triolein 0.83g/Avicel 1.0 g per 10 ml)

	oil content*	% of original oil
Fresh emulsion	0.70 g	84
Freeze -dried	0.75 g	90
After gold coating	0.71 g	85

*Average of 4 samples

It is obvious that no oil is lost during exposure of the dried sample to the high vacuum and heat of the gold evaporator. The reduced recovery of the original oil content is attributed to losses during the separation of the organic phase from the water phase. A white slimy layer is formed at the interface in the maltodextrin system and a layer of avicel in the other system also collects between the two phases.

The above experiment leads to the conclusion that even though the oil is not observed in the avicel samples in the scanning electron microscope using current techniques, it does not mean it is not present in the system. It can be suggested that the oil may be present as a film on the individual cellulose crystals. The results on the maltodextrin samples show that oil is present as inclusions (verified by optical microscopy) and may be also as deposits on the surfaces of the grains.

2.3 Study on Air Incorporated into Freeze-dried Maltodextrin Systems

In order to determine the effect of air on the appearance of the freeze-dried product, the following experiment was conducted:

Aqueous solutions of 10% maltodextrin were prepared. Some aliquots were frozen in liquid nitrogen; the remainder were homogenized in an Omnimixer at maximum speed to incorporate air bubbles in the solution. After 10 minutes homogenization these samples were immediately frozen in liquid nitrogen. After freeze-drying they were examined in the optical microscope and after gold-coating also in the scanning electron microscope.

In the optical microscope no structural differences were observed between the unhomogenized and homogenized samples. None of the samples contained air inclusions.

Representative grains were observed in the scanning electron microscope. The surface of the maltodextrin was very smooth with no cavities, craters, bumps or "eggshells." Broken grains, which were observed at the edge, were completely solid, free of any cavities. A few holes are found along dendritic regions which are caused by secondary or tertiary ice dentrites penetrating the still liquid eutectic phase during freezing. The maltodextrin platelets often exhibit contraction patterns, cracks, and features which look like imprints of ice crystals (often of near hexagonal shape).

The absence of air inclusions in the homogenized samples is most likely due to the air's incorporation at the ice-maltodextrin interface during freezing. In an emulsion system, however, any air present can be locked into the eutectic phase due to decreased mobility caused by the oil globules present in the eutectic and at the interface. Also the presence of emulsifier in the system might aid in the retention of air bubbles in the eutectic phase.

2.4 Microscopy of Oil Containing Aqueous Systems

2.4.1 Introduction

Four groups of oil-in-water emulsion systems have been investigated. These can be differentiated with respect to the matrix forming solute present:

a) maltose

b) microcrystalline cellulose (avicel)

c) maltodextrin

d) urea.

The oil used was either triolein or 1-bromonaphthalene. The emulsions were freeze dried in the microscope freeze dryer (10-15 microliter samples) or in a laboratory freeze dryer (5-10 ml samples), and the dried emulsions were subjected to microscopic investigations.

The emulsions were prepared by blending oil and a low HLB emulsifier together, and adding this mixture to an aqueous solution or dispersion of the solid support and a high HLB emulsifier. This system is then homogenized for 1 to 10 minutes in a high speed Sorvall Omnimixer.

In the freshly prepared emulsions the triolein droplet size is very uniform, around 1 to 2 microns in diameter, though globules up to 12 microns have been encountered. The oil globules are evenly dispersed showing no tendency to flocculate. 1-Bromonaphthalene globules are generally one micron or smaller in diameter, and there seldom are droplets about 5 microns. With 1-bromonaphthalene, a good emulsion can be obtained after about 30 second homogenization.

It has been observed that there is a tendency for a small portion of the oil to cream following homogenization. This is especially true at higher oil phase volumes and in systems without proper addition of emulsifiers. Samples taken for microscopic observations are always taken from the bulk liquid, which means that the actual phase volume will be slightly lower than initially presumed. Following this initial creaming, the remaining emulsion is stable.

2.4.2 Maltose Based Systems

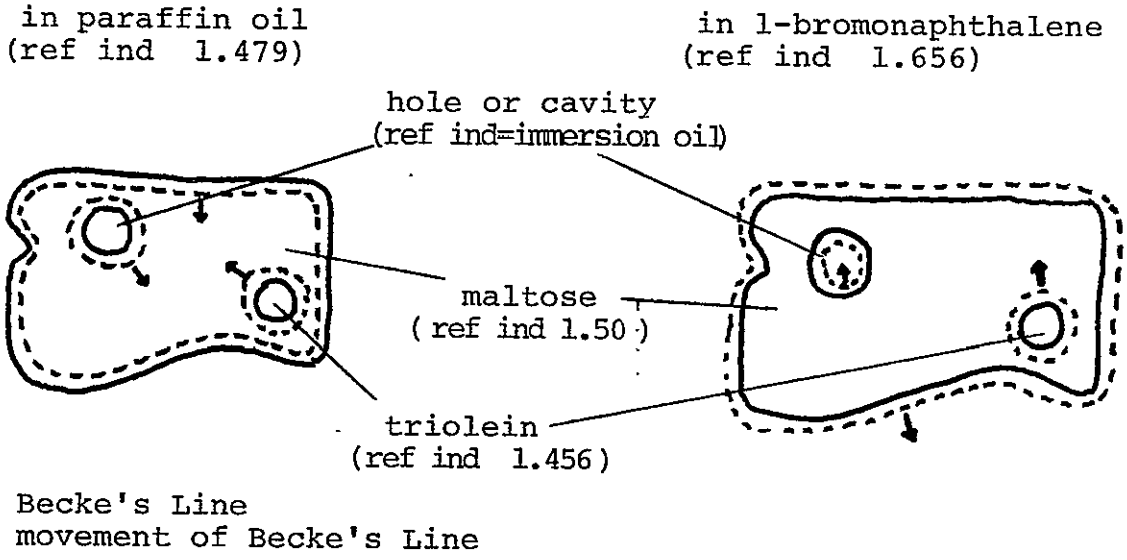
Two sets of triolein-maltose emulsions with triolein phase volumes of 1% and 10%, and a maltose content of 10% were investigated.

In the liquid state prior to freezing, the emulsion had an essentially uniform oil droplet size of about 1 micron, though a few larger droplets of up to 10 microns diameter were noted. The droplets were well dispersed, with no tendency to cluster.

Independent of sample oil phase volume (1% or 10% oil) or freezing rate (slowly at -20°C, or fast by liquid nitrogen immersion) they underwent extensive collapse during freeze drying, both in the microscope freeze dryer and in the laboratory scale freeze dryer. This was very obvious macroscopically by the appearance of glossy areas, foam crusts, and assemblages of yellow areas (oil).

Under the optical microscope, oil inclusions, holes and cavities, and air inclusions were observed for all

samples. The inclusions were spherical, and often "twin" spheres are present, (Figure 3). Oil inclusions are obvious due to their shining black appearance. To distinguish oil inclusions from holes and cavities, the Becke's line method was used in connection with two different immersion oils, one with a refractive index below that of maltose and the other with a refractive index above that of maltose. As the plane of focus passes through the sample (i.e. changing the microscope focus), the Becke's line around an oil inclusion will behave similarly for the two immersion oils, while it will move in opposite directions for holes and cavities. The following illustration shows the phenomena:



In Figure 3 it is seen that oil inclusions have the white Becke's line outside the sphere, while the holes and cavities have the white line inside the sphere (i.e. in

the immersion oil). Since the empty holes have the same shape and size as the oil inclusions, they probably are the remains of an oil inclusion after escape of the oil globule. Supporting this statement is the observation of a maltose wall separating two adjacent spheres, which indicates that oil globules had a tendency to flocculate while being moved in the still liquid eutectic phase during freezing. Some holes can also result from air inclusions.

The larger oil droplets, as observed in the initial fresh emulsions (i.e. sizes larger than 4 microns diameter) were not observed in the dry matrix. Round impressions in the maltose surface which may result from imprints of oil globules up to 6 microns were observed. Dehydration of the samples released oil globules of sizes up to 12 microns suggesting that the oil that cannot be incorporated into the maltose phase is present as thin (apparently invisible) surface deposits.

Scanning electron microscopy could not be carried out since during metal-coating of the sample, structural transformations occurred, apparently due to the heat evolved in the process.

2.4.3 Maltodextrin Based Systems

Aqueous emulsions, which contain maltodextrin as the solid support were prepared using either triolein or 1-bromonaphthalene as the oil component. A typical composition of

a maltodextrin-triolein system is: maltodextrin (10%), triolein (4.6%), Tween 80 (0.4%) and Tween Mos-100vs (0.2%). This composition yields a phase volume relative to water ($\phi_{o/w}$) of 5%. Samples have been investigated with phase volumes of 1% and 10% (maltodextrin 10%) and 5% (maltodextrin 20%).

The fresh emulsions contain oil droplets with an average diameter of about 1 micron, though a few larger droplets of up to 10 to 15 microns were noted. The droplets were well dispersed without noticeable tendency to flocculate.

In the optical microscope the oil is observed in the freeze dried system as spherical inclusions of sizes up to about 5 microns. "Fett Rot"-dyed triolein appears clearly visible in the microscope. Small inclusions (less than 1 micron diameter) do not appear red or spherical due to physical limits of the resolving power of the microscope, which is about 0.6 microns. This is important to remember, especially when quantitative measurements on oil content will be made, since the small round features (inclusions) can in actuality be dust particles, micro organisms, air, etc.

Fig. 4 gives a view of the variety of surface morphology of a freeze dried 1% triolein - 10% maltodextrin grain.

The following features can be observed:

1) folds after ice dendrites
2) cracks

3) holes, presumably due to ice crystal punctures during freezing
4) craters, from escaped oil or air at the ice/solute interface following freezing
5) bumps, covering over oil inclusions
6) microorganisms

Figure 5 shows a crater at large magnification. The spherical shape is evident, which is demonstrated by the curved crater side and the hole in the bottom. This is probably the imprint of an oil globule that had a larger diameter than the thickness of the carbohydrate. It was sticking out on both sides of the grain and the maltodextrin couldn't cover the poles which were in direct contact with the ice. Upon sublimation of the ice, nothing held the oil in place and it presumably leaked out covering the surface as a film deposit. This type of crater is generally observed when viewing most dried emulsions by scanning electron microscopy and also at times with the optical microscope, especially with gold-coated samples where a shadowing effect is obtained.

Other types of holes which lack a crater rim are also observed. These most likely are due to punctures caused by growth of secondary and tertiary ice dendrites during freezing, since they also can be found in freeze dried maltodextrin solutions containing no oil.

Studies using both optical and scanning electron microscopes have allowed differentiation of a number of morphological structures in an emulsion based on 1-bromonaphthalene, maltodextrin and water, with a mixed Tween emulsifier system. The composition was: 1-bromonaphthalene (10%), maltodextrin (20%) and 0.5% emulsifiers (Tween 80 and Tween Mos-100vs in the ratio 2 to 1). The original fresh emulsion had an average droplet size of less than 1 micron. The freeze dried emulsions were very crisp and non-sticky indicating good encapsulation of the oil in spite of the high phase volume.

In one series of samples it was possible to distinguish between areas in which lipid droplets were very tightly packed and other areas in which the droplets were present at a much lower "density." In the first case the oil inclusions had lost their spherical shape, figures 6 and 7, while in the second case they appear as nice regular spheres (Figure 8). Figures 7 and 8 are scanning electron micrographs showing a view of a broken edge of a sample, thereby allowing the inclusions to be seen.

In those regions where the droplets were tightly packed, it can be expected that coalescence will be much more likely to occur.

In another sample, the sequential studies again demonstrated the value of utilizing both techniques. While the SEM allowed a good visualization of the overall struc-

ture of the maltodextrin grain, it was only in the optical microscope that the inclusions could be observed, and partially identified as being 1-bromonaphthalene by refractive index measurements. By the same technique it was discovered that the Tween 80 emulsifier also appears as inclusions in the matrix (Figure 9). Note that in this humidified sample (same view of sample as Figure 6), the 1-bromonaphthalene appears dark with Becke's line outside the drop while the Tween 80 appears lighter and the Becke's line is inside the drop, since the maltodextrin phase has a refractive index intermediate between that of the respective droplets.

The discovery of the Tween 80 inclusions was quite unexpected and is indicative of emulsion destabilization during freezing and may be a cause for the tendency for the oil droplet size distribution of an emulsified system to increase following freeze-thaw cycles. It could also be due to poor solubilization of the Tween 80 in the water prior to emulsion preparation and freezing. It was not possible to observe a separate phase of the Tween Mos-100vs, the other emulsifier.

In addition to the 1-bromonaphthalene and Tween 80 inclusions, it was possible by optical microscopy to observe:

1) air inclusions in the matrix
2) holes in the matrix presumably due to ice crystal puncture during freezing

3) "imprints" of lost oil globules or air bubbles.

Surface morphology as observed in the SEM showed numerous bumps, holes, and craters which may be due to either oil droplets or air bubbles. In the case of holes they might also be impressions from ice crystals as previously discussed.

2.4.4 Microscrystalline Cellulose Based Systems

Some studies using avicel, a microcrystalline cellulose as the solid support were reported in the Phase II Annual Report. In the present study, sample composition of either 1% triolein with 10% avicel or 10% triolein with 10% avicel were emulsified in a high speed mixer. In the liquid state oil droplets and insoluble cellulose microcrystals are observed. Also present is a component which is difficult to resolve in the optical microscope and is presumed to be broken microscrystal units. The oil droplet size ranges from 1 to 10 microns.

In the dried systems, the presence of droplets is difficult to observe due to their low number. The amount noted is much less than that which should be present based on initial oil phase volumes and avicel concentration. Rehydration of the dried samples causes an abundance of oil droplets (1 to 10 microns diameter) to be visible, free-floating as well as attached to the microcrystals.

In the scanning electron microscope the cellulose crystals appear as rods with a very wrinkled surface. The small pieces, presumed to be shredded cellulose crystals, appear to have a bridging effect between the larger crystals resulting in a dense matrix structure (Figure 10). Small 2 to 4 micron empty shells have tentatively been interpreted as cellulose crusts enveloping escaped oil globules but this would only account for a very small fraction of the total original oil content. That the oil <u>is</u> present in the dried system can be demonstrated since rehydration of a gold coated sample liberates numerous oil globules (~10 microns diameter). The oil is presumably present as a film coating the cellulose crystals. More work is needed, however, to demonstrate this as the location of the fat.

2.4.5 Urea Based System

Most studies to date have been conducted using carbohydrates which freeze dry in an amorphous state.

In response to a report which claimed that urea-based freeze dried emulsions showed the lipid phase in the form of droplets external to crystalline needles of urea, a few experiments utilizing urea as the solid support were undertaken.

It is reported that while pure urea crystallizes as a tetragonal system in forming inclusion compounds with straight chain organic substances (i.e. fatty acids)

it crystallizes in a hexagonal system. Initial experiments were initiated to determine if the differences in behavior of the crystalline urea system for different lipid constituents could be utilized for interpretation of the structure of the oil-urea freeze dried matrix.

Samples were prepared by adding the following lipid materials to a methanol solution saturated with urea:

a) no lipid present

b) triolein

c) linoleic acid

d) triolein and linoleic acid.

The oil concentration was about 3% of the urea-methanol solution (which had been decanted from the saturated solution so that no undissolved urea was present). No precipitation of urea was noted in the lipid-free samples, unless some of the methanol was evaporated.

Triolein was not solubilized by the methanol and was present on the bottom of the flask as distinct oil globules around which there was a slow precipitation of urea during a 24 hour period. In the linoleic acid sample, precipitation was rapid, occurring within a minute. The triolein-linoleic acid sample acted similar to the linoleic alone except that the triolein did not dissolve. A microscopic investigation of urea crystals recovered from the methanol solutions showed a distinct difference in crystal morphology. The pure urea formed short rods

while the oil containing urea samples appeared as long slender needles with visible oil inclusion. Dissolution of the urea crystals in water releases oil globules of larger sizes than observed in the needles.

These observations show, as expected, that linoleic acid, and to a lesser extent triolein, form urea adducts. In the system composed of triolein and linoleic acid, needles of urea were formed with visible oil inclusion.

Urea freeze dries to give a crystalline solid. This can be easily demonstrated by means of polarizing filters in the optical microscope. Pure urea freeze dries forming clusters of short rods ($L/D \sim 2$) or needles ($L/D > 3$). The morphological pattern of the urea crystals is constrained by the limited growth space in the eutectic caused by the already formed ice crystals and therefore comparisons of the crystal morphology of these freeze dried samples with the above mentioned oil-urea-methanol systems should be done very cautiously. Freezing rate, which influences solid phase grain size, must also be taken into consideration. When aqueous solutions of urea (20%) containing dyed triolein (1%, 3%, 5%) were freeze dried, small oil droplets (diameters $\leq$ 1 micron) were observed to be trapped <u>within</u> the crystalline structure (Figure 11). These oil droplets were not dissolved when the dried urea samples were suspended in fat solvents, such as hexane or chloroform, etc. It was observed that

addition of water, which gave solution of the urea crystals, results in the appearance of large numbers of oil droplets having a wider range of diameters (up to 10 microns) than has been observable.

The appearance of oil not previously observed in the dry state suggests that a fraction of the original oil may be present as either a thin coating around the individual urea particles, or that the oil is forming urea adducts. The observed stickiness of the dry particle suggests that the oil is on the surface.

Gold-coated samples of the triolein urea freeze dried systems were observed in the SEM (Figure 12). A few bumps in the 1 to 2 micron size range were found and presumably indicate underlying lipid inclusions. The oil-free urea system does not show any appearance of bumps or other surface irregularities. The bumps were not numerous enough to account for all the oil inclusions observed in the optical microscope. This suggests that some of the oil droplets are imbedded deep inside the crystalline urea plates. Craters with circular circumference are observed in sizes up to 10 microns, and they may represent imprints of oil droplets trapped at the ice-urea interface following freezing.

Freeze dried aqueous samples of urea (20%) and stained linoleic acid (1%, 3%) show very much the same morphological patterns as mentioned above for triolein-

urea. The urea forms needle-like structures with lipid inclusions generally 1 to 2 microns in diameter. Addition of water releases oil globules with much larger diameters than observed in the dried samples. Sizes up to about 12 microns in diameter were observed. It appeared that the linoleic acid systems contained fewer visible droplets than the corresponding triolein systems which is not surprising considering the potential for adduct formation as mentioned above.

List of Figures

shell" presumably due to escaped oil or air inclusion)

Figure 6 Optical microscope view of freeze dried emulsion of 1-bromonaphthalene (10%) and maltodextrin (20%) in dry state showing inclusions of 1-bromonaphthalene (light grey to right), Tween 80 (darker grey to center) and air (dark areas to far left)

Figure 7 SEM view of same sample as Figure 6. View of broken edge showing imprints of oil inclusions in "crowded" region.

Figure 8 SEM view of same sample as Figure 6. View of broken edge showing imprints of oil inclusions in "uncrowded" region.

Figure 9 Optical microscope view of same optical field as Figure 6 after humidification at 43% RH. Inclusions of 1-bromonaphthalene (light rim, dark interior) and Tween 80 (dark rim, light interior) present as droplets in viscous matrix.

Figure 10 SEM view of freeze dried emulsion of triolein (1%) and Avicel (10%)

Figure 11 Optical microscope view of freeze dried emulsion of triolein (5%) and Urea (20%) showing triolein inclusions in individual urea needles.

Figure 12 SEM view of freeze dried emulsion of triolein (5%) and Urea (20%) showing imprints at broken edges of triolein or air.

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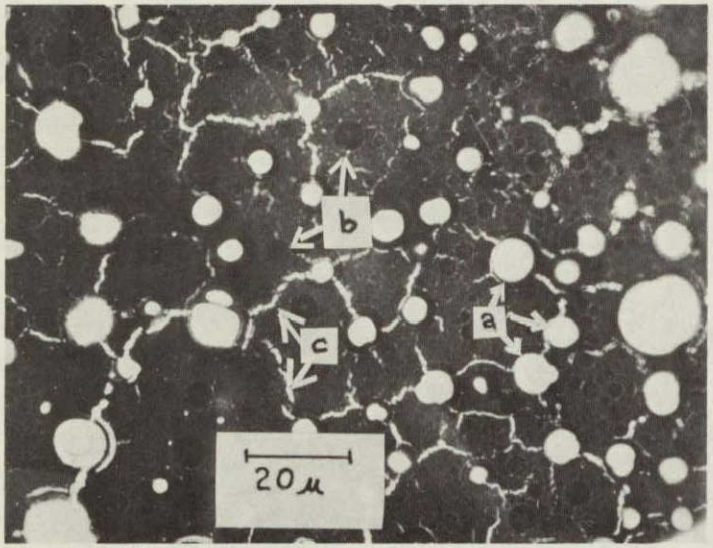


Figure 1

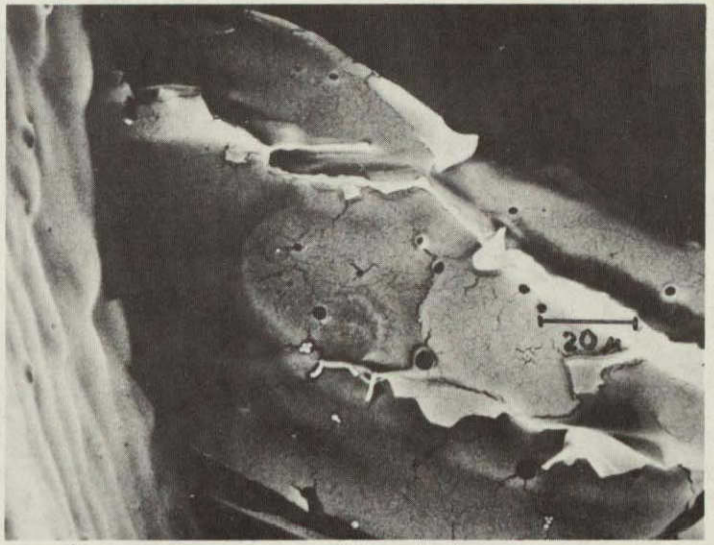
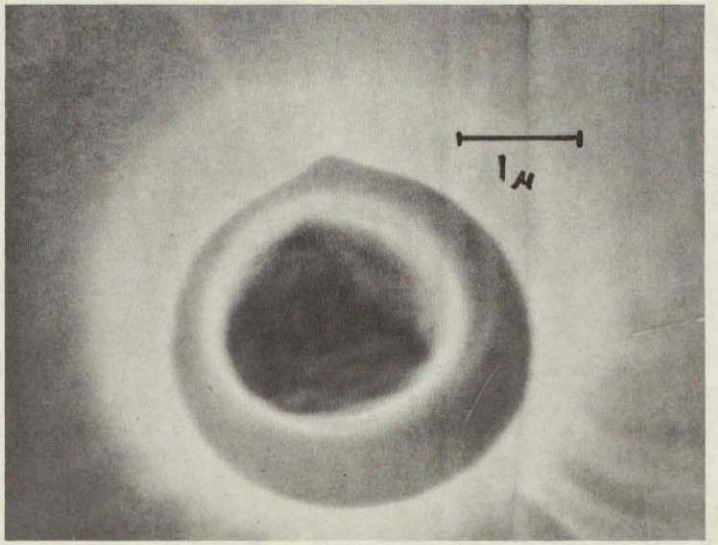


Figure 4

Figure 3



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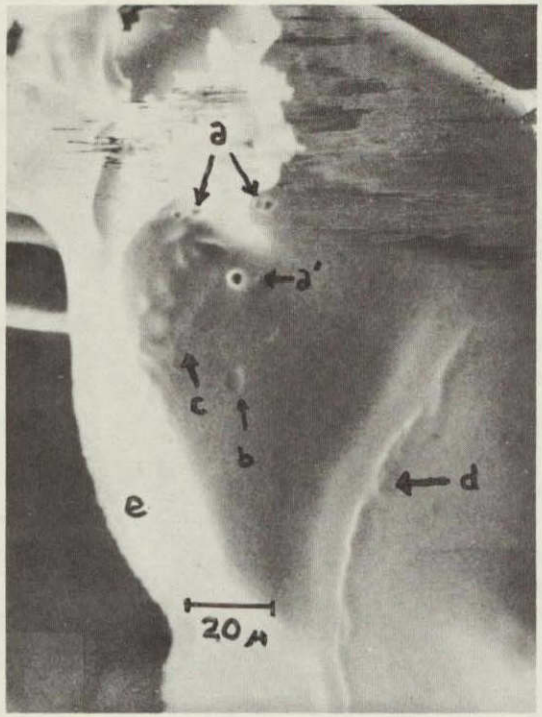


Figure 2a

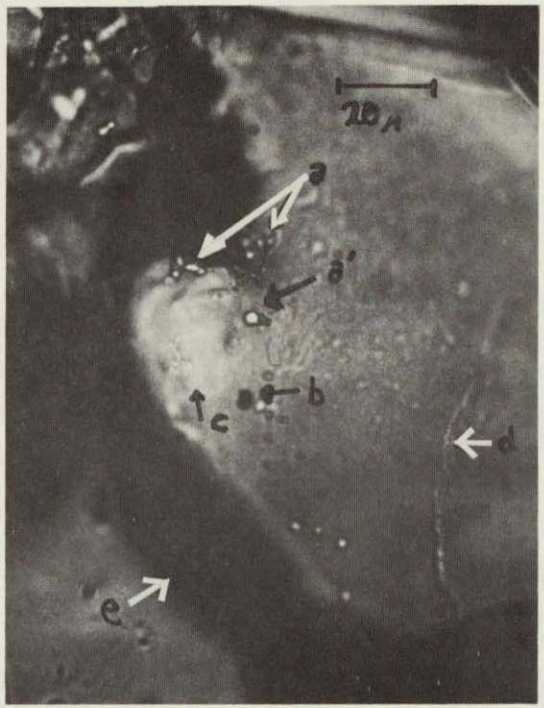
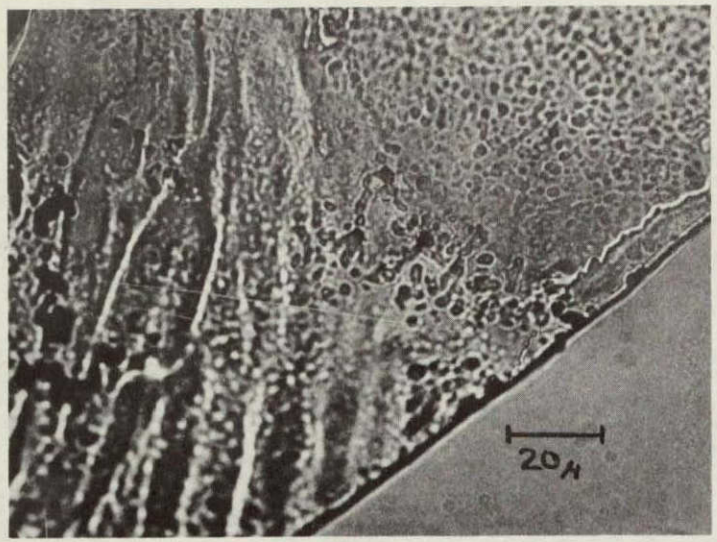


Figure 2b

a) holes
a') hole next to Tween 40 inclusion
b) bump over air inclusion
c) bumps over 1-bromonaphthalene
d) ridge
e) maltodextrin wall



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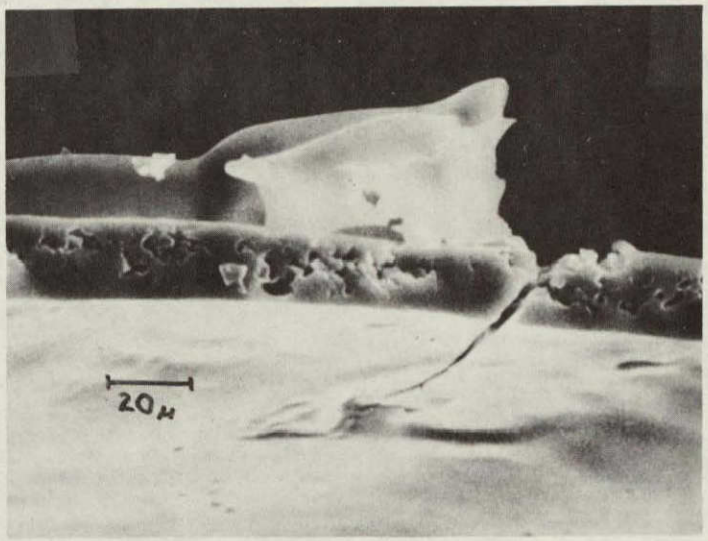

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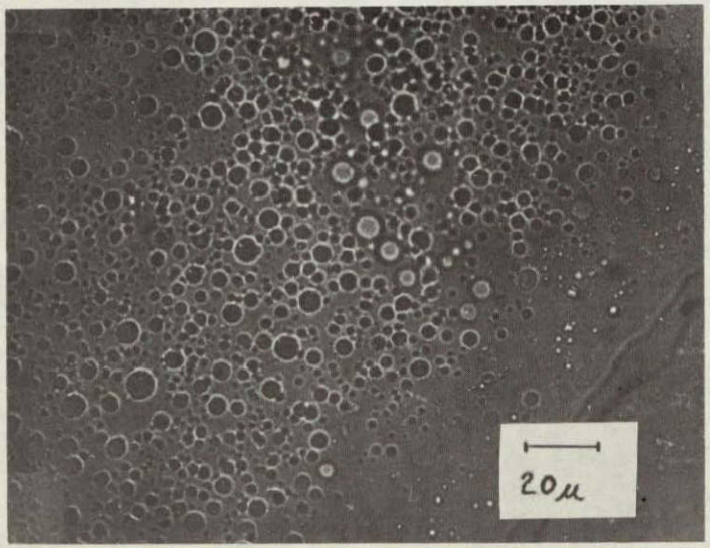

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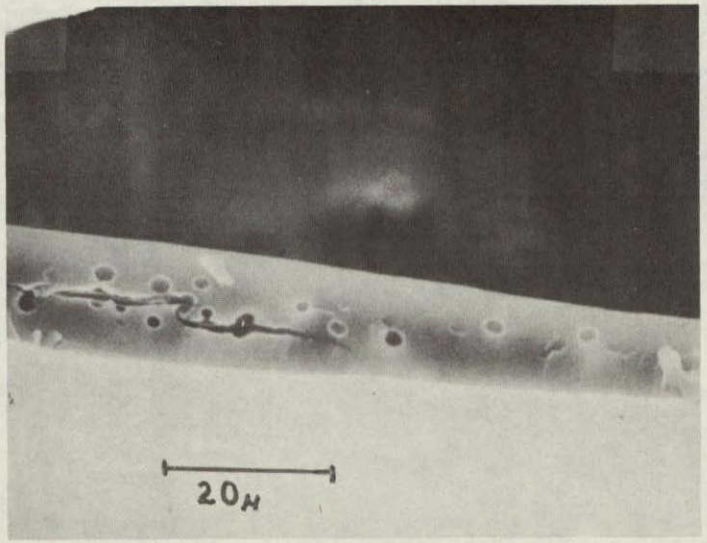

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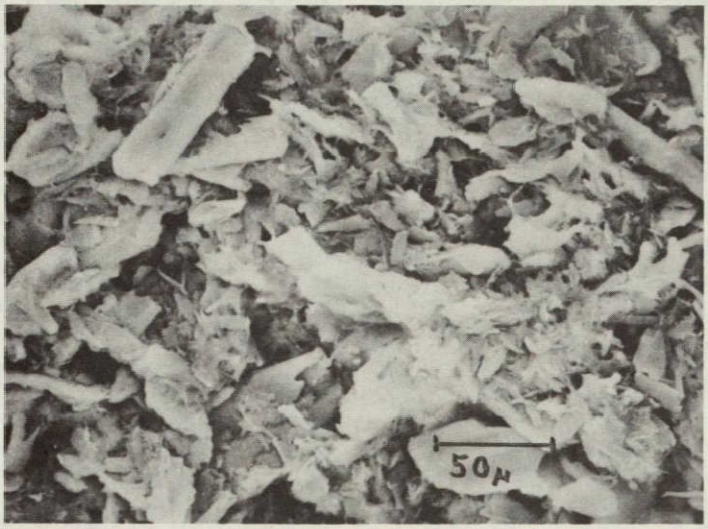

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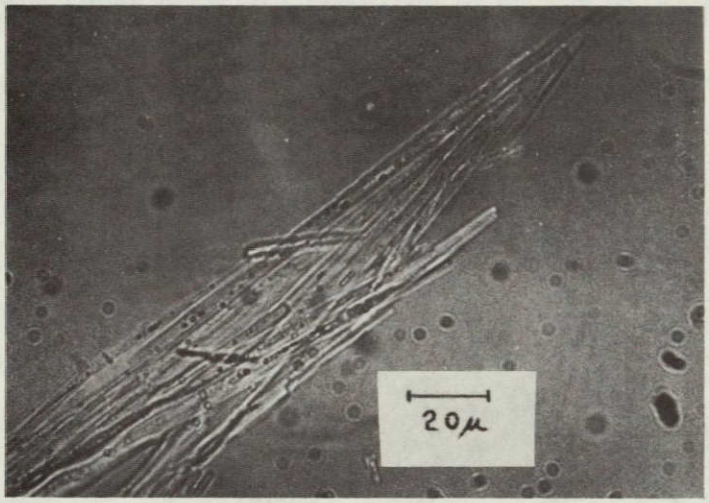

Figure 11

Figure 12

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3. Browning of dried foods at high temperatures

3.1 Introduction

In a continuation of work reported upon in the Phase I and II Annual Reports, we have investigated the high temperature susceptibility to browning of some dried food products, especially nonfat milk. As has been noted in earlier Annual Reports, exposure of food materials during freeze drying to high temperatures, especially in the second (desorption) phase of freeze drying, will result in nutritional and organoleptic deterioration. Temperature problems associated with the Skylab launch indicate the wider need for information regarding high temperature stability of dehydrated food products during storage. It is fortuitous that the same range of heating temperatures is applicable to both the study of product deterioration during the desorption phase of freeze drying and the high temperature storage stability of dehydrated products.

In a continuation of the work conducted in Phase II of this contract, most studies were conducted using nonfat dried milk. This product is easily available and represents a highly susceptible system. Further, analytical procedures for evaluating brown color formation in dried milk are well known. As a result of the Skylab temperature problem, it became apparent that dehydrated eggs were particularly susceptible to high temperatures, and evaluations using this product were also continued. In this case,

analytical techniques are not so well defined, and some effort has been expended in developing a quantitative technique for evaluating brown color which can correlate with qualitative visual differentiation of treated samples. The procedures have been improved but are still not fully satisfactory.

In some tests, evaluation of degradation of product color and quality due to high temperatures were conducted with heating of the samples occuring either during freeze drying or after the dried product was removed from the freeze dryer. These studies were conducted using both nonfat milk and fruit slices.

A technical paper on some aspects of the nonfat dry milk work, entitled "Some Properties of the Freeze Drying 'Scorch' Temperature" was presented at the 1974 Annual National Meeting of the Institute of Food Technologists at New Orleans, and recently appeared in the Journal of Food Science. A copy of that paper is appended to this section.

3.2 Studies on Browning of Nonfat Milk

3.2.1 Methods

Commercially available spray-dried nonfat milk powder is used as the raw material. This is generally reconstituted to 20% solids and aliquots of the solution pipetted into 50 ml erlenmeyer flasks (20% solids represents a concentration representative of concentrated food liquids prior to freeze drying). These are frozen in liquid nitrogen and freeze dried. Freeze drying can be with room temperature platens or at elevated temperatures depending on the experimental goals. Following freeze drying, samples to be humidified are placed in desiccators over saturated salt solutions of constant water activity for 24 hours at 37°C. The flasks are then tightly sealed with rubber stoppers and heated in air at the desired temperatures.

Brown color was measured spectrophotometrically on an aqueous extract of the milk powder. The procedure is as follows:

1) Add 20 ml distilled water to 2 g of dry sample in a 50 ml erlenmeyer flask.

2) Add 2.5 ml of a freshly prepared 10% trypsin solution to each flask and stopper.

3) Hold each sample for 1 hr in a 45°C water bath, with shaking.

4) Following incubation, add 2 ml of a 50% Trichloroacetic acid solution to each sample.

5) Add about 0.1 g of Celite Filter Aid to each sample.

6) Filter the samples through either S+S #576 or Whatman #42 ashless filter paper.

7) Any solutions which contain suspended material should be centrifuged.

8) The clear solutions are read at 450 nm using a treated trypsin solution as the blank.

9) Browning value is calculated as $\frac{O.D._{450} \times 100}{\text{dry sample weight}}$

(On a few occasions, optical density was measured at 420 nm; tests showed that while absolute levels of browning values differed from those determined at 450 nm, either wavelength gave similar indications of browning behavior.)

3.2.2 Sample Geometry and Browning Behavior

Two studies considered the influence of sample geometry on extent of browning. In one, browning was investigated by comparing browning values of nonfat milk prepared as chunks (approx. 3mm cubes) or as a powder (to pass a 40 mesh sieve, 420 µm openings). These samples were humidified and then heated at 90°C for 4 hours. While some changes in weight during heating were observed, it was possible to evaluate the browning data for the powders and chunks by plotting browning value against sample moisture content. Figure 1 shows plots for samples humidified at 32% R.H. It can be seen that there is a sizable difference in browning for the powder and chunks, most probably related to effective heat transfer within the sample. This difference was not noted for samples humidified at 11% R.H.

Milk samples were frozen in layers and then freeze dried at elevated heating temperatures. Upon completion of the freeze drying, the layers were separated and analyzed for brown color. The most severe browning occurred at the surface and a gradient of color was observed from the surface to the sample center. Similar behavior was observed in unlayered samples, and a comparison of average browning values for layered and unlayered samples showed good agreement, indicating that the layered samples behaved similarly to regular samples. (Table 1)

These results indicate that the particle size, in so far as it influences the time for which the surface is exposed to high heating temperatues, will be very important. Additionally, it appears that in the practical case of radiant energy freeze drying, where the highest sample temperatures occur at the regions of lowest moisture content, the local sample temperatures will be more critical than moisture content.

3.2.3 Browning Behavior During Freeze Drying

In the previous section it was noted that differences in extent of browning occurred during freeze drying. The behavior of nonfat milk towards browning was evaluated in a few studies in which drying parameters were varied.

In one study, milk samples were freeze dried at 3 constant heating platen temperatures, 84°C, 100°C and 120°C. Browning values, weight loss and sample temperatures were evaluated as a function of time. These tests showed that

it was possible to dry milk in 2 hours by heating at 100°C. Following freeze drying, evaluations of browning have been conducted using both visual organoleptic and spectrophotometric determinations (Table 2). The color was acceptable even though the sample had reached 100°C during the drying process. At 120°C, an unsatisfactory level of browning had occurred. The results of this test are incorporated as Table 2 of the technical paper included in this section (see page 3-11).

Subsequent studies on high temperature tolerance (relative to brown color formation) during freeze drying utilized a freeze drying chamber (designed and constructed at M.I.T.) which allows better control of heater and sample temperatures, as well as permitting continual determination of sample weight. The time dependence of weight loss and sample surface temperatures of nonfat milk being freeze dried at various constant heating platen temperatures are shown in Figures 2 and 3. Even though the samples were exposed to high temperatures, very little browning was observed at heater temperatures up to 110°C. Above this level, some browning of the upper surface was noted. If the samples were crushed prior to evaluation, the samples were virtually indistinguishable visually, and spectrophotometric measurements depended strongly on sample uniformity (i.e. uniform mixing of surface layer) prior to extraction.

While most studies on freeze drying of nonfat milk samples in the new freeze drying chamber have been conducted with 200 ml samples (approximately 12 mm thickness) at a 20% solids concentration, the effect of varying solids concentration and sample thickness was investigated. The basic results are also presented in Table 3.

The importance of solids concentration on rate of production can be easily seen, and that browning does not increase linearly with throughput when solids content is varied.

3.2.4 Quality Evaluations of Dry and Rehydrated Samples

Further evaluations on changes in the properties of nonfat milk following heating have been conducted in the areas of visual ranking of the rehydrated product, a correlation of results of this test with browning value, a qualitative evaluation of solubility of the powder, and a taste evaluation. The visual ranking of dry and rehydrated milk correlates well with browning value, and the order of ranking does not appear to vary greatly between dry and rehydrated samples. Powder solubility was evaluated when rehydrating the samples and a value was assigned using a scale of 1 (as soluble as instantized spray dried milk) to 10 (slightly soluble). Solubility values ran from 2 to 7 and could be correlated with browning value (Table 4).

3.2.5 Reprint of "Properties of the Freeze Drying 'Scorch' Temperature"

Reprinted from Journal of Food Science.
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PROPERTIES OF THE FREEZE DRYING "SCORCH" TEMPERATURE

INTRODUCTION

IN RECENT YEARS a number of studies have been reported on mathematical simulation of the freeze drying process (Sandall et al., 1967; Dyer and Sunderland, 1968; Cho and Sunderland, 1970; Aguilera, 1973). An integral part of most of these studies has been the inclusion of a maximum temperature value for the dry region, generally called the "scorch" temperature, maximum allowable dry layer temperature, maximum surface temperature and so forth. In all cases, the attempt is to define a product temperature which marks the transition from an acceptable to an unacceptable product, with product quality generally related to the formation of dark color (hence, "scorch" temperature). While it is well recognized that browning is time and moisture, as well as temperature dependent, it is presumably the ease of measuring and controlling temperature that promotes considering browning from a temperature-only approach.

The kinetics of browning reactions have been widely studied for many model systems and food materials. However, these studies have tended to concentrate on determination of reaction mechanisms or storage stability of foods, including dehydrated products. Indeed, it seems likely that most reported values of the "scorch" temperature are developed from storage studies, and thus are very low, having severe economic implications on the cost of freeze drying (Flink and Fosbøl, 1972). There appear to be very few studies on browning occuring *during* dehydration processes, especially freeze drying. One notable exception for freeze drying is a study on browning kinetics using a glucose/glycine mixture deposited upon cellulose (Kluge and Heiss, 1967). In these studies, browning kinetics and drying behavior were combined to develop times at which a level of browning, arbitrarily chosen to be the limit of acceptability, was achieved.

In recent work on computer simulation of continuous freeze drying (Aguilera, 1973; Aguilera and Flink, 1974a, b), methods have been developed to obtain local values of temperature and moisture. This information can be used with browning kinetics to develop integrated levels of browning during the freeze drying process for inclusion into any process optimization procedure.

This paper reports on a study of browning kinetics at high temperatures and low moisture contents, as might be found in the dry layer during a freeze drying process. Additionally, a visual organoleptic assessment of these browned materials is presented.

MATERIALS & METHODS

Sample preparation

An aqueous model system of glucose, glycine and avicel (microcrystalline cellulose) was well mixed (usually at concentrations of 8.3%, 8.3% and 3.3%, respectively), placed into plastic petri dishes, frozen in liquid nitrogen and freeze dried under gentle conditions (ambient heating, <0.1 torr).

Nonfat dry milk samples were prepared by reconstituting commercial spray dried milk powder as a 20% solution, placing it in various sample holders, freezing in liquid nitrogen and freeze drying, again under gentle conditions

Thermally induced browning

Samples to be humidified prior to browning were exposed over saturated salt solutions for 24 hr at 37°C Humidified samples were heated in sealed Erlenmeyer flasks to prevent loss of water. Gravametric measurements were recorded to monitor sample moisture contents. Samples were heated in constant temperature ovens for various times.

Organoleptic assessment of browning

The heated samples were crushed and sieved to give a uniform particle size and untrained judges were asked to rank the samples in order of increasing darkness, and to choose the dividing line between acceptable and unacceptable samples These same judges were later asked to evaluate each sample individually as to its acceptability An analysis of variance test (Larmond, 1970) was applied to the ranked data to determine significance of difference between samples.

Quantitative assessment of browning

For milk samples, an extract of the brown color was obtained from the samples following a trypsin digestion and TCA precipitation of the proteins (Choi et al., 1949). The clear solution, following filtration and/or centrifugation, was read at 450 nm using a trypsin solution as a blank. Browning values (BV) were calculated as 100 times the optical density divided by the weight of powder extracted.

For the glucose/glycine model system, the water extract was obtained without the trypsin digestion or TCA precipitation. The OD of the centrifuged extract was read at 400 nm and the browning value given as OD per 0.3g of solids.

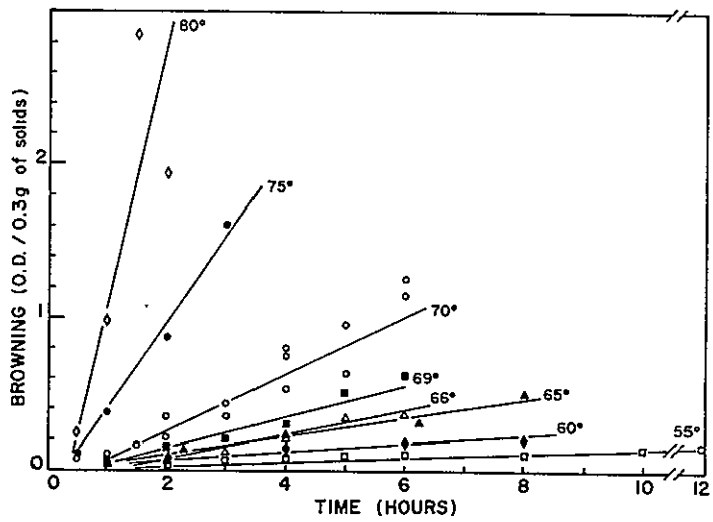

Fig. 1—Browning of freeze-dried glucose/glycine/avicel model system heated at various temperatures.

RESULTS

INITIAL STUDIES on dry samples showed no difference in browning values when heating was conducted with the oven under vacuum or at 1 atmosphere pressure. Studies on humidified samples, sealed in ampoules under air or vacuum, again showed no difference in browning values. Based on these tests, the simpler procedure of air heating of sealed sample vessels was adopted, rather than that of heating under vacuum, which would have been a truer model of freeze drying conditions.

Figure 1 shows the results for heating of the dry glucose/glycine model system. For temperatures below about 65°C little browning occurs. Above 65°C a rapid rise in browning rate occurs. Similar behavior was noted with the milk samples. Browning values for samples equilibrated at 32% RH are shown in Figure 2, while samples at 0% and 11% RH are given in Figure 3. Again, it can be seen that browning rates accelerate as the temperature increases. In Figure 4, the rates of browning are shown to increase sharply at "critical" temperature levels which apparently depend on the sample water activity. The sharpness of these curves indicates that both sample temperatures and moistures will be important in determining sample browning behavior. Arrhenius plots were used to calculate the energy of activation of the browning reactions (Figure 5). These energies were determined to be 47, 53 and 33 kcal/mole for samples at 0%, 11% and 32% RH, respectively.

Visual and spectrophotometric evaluations of sample browning are given in Table 1. The ranking is ordered according to visual rating, and it can be seen that it is difficult to correlate visual and spectrophotometric ranking for light samples.

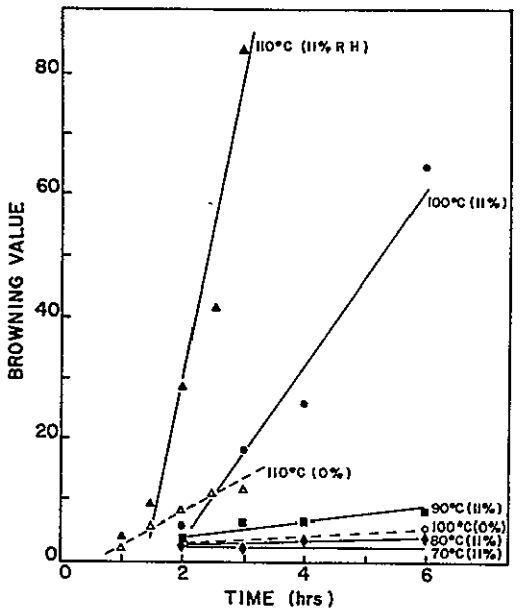

Fig. 3—Browning of freeze-dried nonfat milk humidified at 0% or 11% RH and heated at various temperatures.

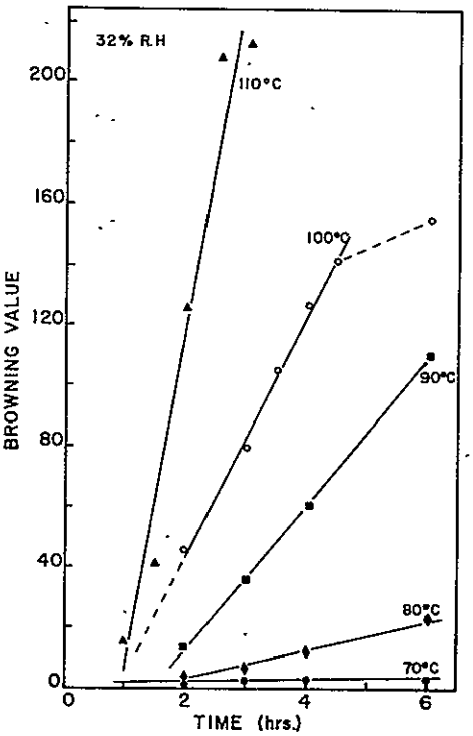

Fig. 2—Browning of freeze-dried nonfat milk humidified at 32% RH and heated at various temperatures.

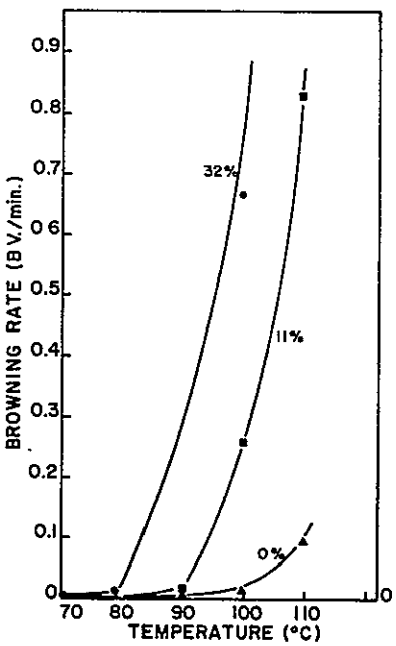

Fig. 4—Rates of browning of freeze-dried milk for heating treatments at various water activities.

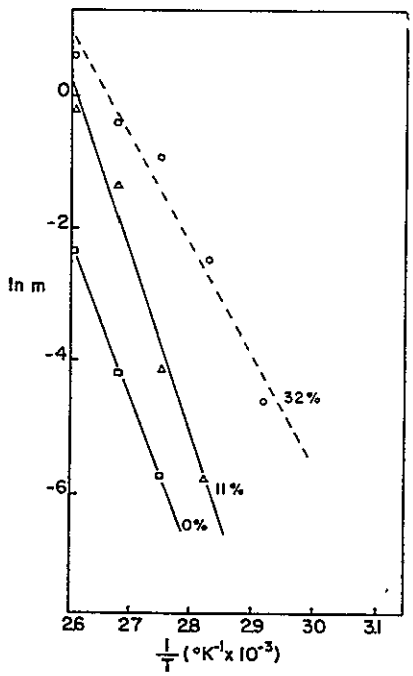

Fig. 5—Arrhenius plots for browning of freeze-dried nonfat milk at various water activities.

Table 1—Visual and spectrophotometric evaluation of browning of dried milk heated at 90°C

Ranking by visual test[a]		Browning value[b]
32/6	a	109.5
32/4	b	49.6
32/3	c	23.2
11/6	d	8.4
Acceptability limit — independent judgements		
32/2	d,e	10.4
11/2	e,f	5.4
Acceptability limit — group judgements		
11/3	f	4.5
00/4	g	1.39
00/6	g	1.06
00/3	g	0.96
32/0	h	2.40
11/2	h	3.50
11/0	i	1.82
00/2	i	0.27
00/0	i	0.31

[a] Sample code (relative humidity/hr of heating). Samples with same letter are not ranked differently at the 5% level.

[b] Browning value is $\frac{(OD_{450})(100)}{\text{g dry solids}}$.

Table 2—Extent of drying and browning values for three heating temperatures during freeze drying[a]

Time	84°C			100°C			120°C		
	Fractional drying[b]	Temp[c]	BV[d]	Fractional drying[b]	Temp[c]	BV[d]	Fractional drying[b]	Temp[c]	BV[d]
1	0.51	35	2.83	0.58	64	3.19	0.78	75	2.03
1.5	—	—	—	0.91	96	3.45	0.87	114	3.97
2	0.87	60	2.31	1.00	100	4.30	1.00	120	18.34
4	1.00	84	2.78	—	—	—	—	—	—
Avg initial moisture content	80.57			80.64			80.60		

[a] Samples 5 mm thick, heated by radiation from two sides, moisture loss from one side

[b] Fraction drying = $\frac{\text{wt lost}}{\text{initial moisture}}$.

[c] Surface temp

[d] Browning value = $\frac{(OD_{450})(100)}{\text{g dry solids}}$.

Concerning product acceptability, the product is judged acceptable even after substantial heating at low water activity. When the samples are presented individually rather than in a group, a significant rise in the range of acceptable browning values occurs.

DISCUSSION

THE RESULTS presented above have shown that browning which occurs at conditions simulating freeze drying is strongly temperature-, moisture- and time-dependent, indicating that a unique value of "scorch" temperature is not realistic and that, to the extent possible, moisture and time parameters should be included in consideration of product quality changes due to browning. This is especially true when heat and mass transfer occur through the dry layer (radiant heating or heating of granules) since regions of high moisture content have the lowest temperatures and regions of high temperatures have the lowest moisture contents.

The results also indicate that dry materials can be heated to quite high temperatures for durations significant when compared to typical freeze drying processes without "unacceptable" changes in visual quality occurring. When products are not visually compared, as would occur in the consumer market, the level of browning which is visually acceptable almost doubles (in browning values). An interesting sidelight is that the original spray-dried powder had a yellowish tinge due to the glassy surface of the particles which resulted in its being always ranked "unacceptable" even though it had the lowest browning value. The freeze-dried powders had a much more reflective surface, making them appear much whiter.

Table 2 gives the fractional extent of drying and browning values for three heating temperatures, showing that high heating temperatures can be used in freeze drying milk powder and result in an acceptable product. The levels of acceptability given in Table 1 show that samples of milk freeze dried at a constant heater temperature of 100°C could be completely dried in 2 hr with an acceptable level of browning.

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3.3 Studies on Browning of Whole Egg

Studies on browning of freeze dried whole egg powder have continued. Various methods for quantifying the extent of browning have been investigated, though the complex nature of the browning reaction in whole egg has made this difficult. In particular, correlation of browning values with visual ranking is difficult because the initial action is for the heated egg to lighten in color prior to the time at which formation of the brown pigments begin.

3.3.1 Methods

Spectrophotometric and spectrofluorometric methods based on organic solvent extraction of the whole egg powder or salt extracts of the defatted egg powder have been evaluated. Most fat extractions have been conducted with chloroform, though petroleum ether has been investigated because it can tolerate a centrifugation step without loss of volume due to evaporation.

Evaluation of the absorption spectra for chloroform extracts from heat treated egg samples led to the choice of 390 nm for determination of a browning value.

The procedure is given below for browning measurements using the lipid extract.

1) 3.0 g of whole egg powder is weighed into a 50 ml erlenmeyer flask.

2) 35 ml of either chloroform or petroleum ether is added to the flask, which is then shaken for 20 min.

3) Samples are then suctioned filtered and rinsed twice with 10 ml portions of chloroform. (If PET ether is used as solvent this step is replaced with a centrifugation step).

4) Repeat steps 2. and 3.

5) The combined extracts are read at 390 nm.

6) The defatted powder is desolventized and saved for further analysis (see below).

It has been shown previously that extracting the defatted powder with KCl gives a solution whose fluoresence shows a peak value at some intermediate time of heating, when this heating is conducted at high temperatures. This most likely indicates the breakdown of some intermediate or otherwise unstable compound, and thus, while flavor evaluations have been shown to correlate with fluoresence values, brown color will not.

The salt extraction procedure utilized is given below.

1) 1.0 g of defatted egg powder is weighed into a 125 ml erlenmeyer flask.

2) 100 ml of a 10% KCl solution is added to the flask and shaken for 30 min.

3) Samples are gravity filtered through 2 layers of #589 filter paper.

4) The clear extracts are read either spectrofluorometrically (excitation at 365 nm and emission at 450 nm) or spectrophotometrically (at 280 nm).

To evaluate if residual brown color was bround by the egg proteins of the defatted cake, trypsin digestions were conducted. No improvement in color extraction was observed.

3.3.2 Results of Egg Browning Studies

The extents of browning as a function of heating time are presented for three analytical approaches. Figure 4 gives the browning value as determined by reading optical density at 390 nm of the chloroform extract of the whole egg powder. Figure 5 shows the % emission (related to concentration in extract) for the KCl extract of the defatted egg powder. It can be noted that these values appear to reach a maximum (for example heating at 110°C) and then decrease indicating that the procedure is measuring some intermediate of the overall reaction.

The salt extracts were also evaluated spectrophotometrically and showed an absorption peak at 280 nm, which appeared to be related to extent of heating. Figure 6 presents absorbance values for KCl extracts measured at 280 nm. The values appear to reach a maximum value when heated at the higher temperatures. From the wavelength of the adsorption peak it is considered that these measurements are probably related to degradation of protein, rather than browning.

The browning values based on fat extraction appear to provide the best correlation with visual evaluation.

Browning values increase with heating time, at first rapidly and then at a slower rate (Figure 4). When the measured browning values are correlated with visual organoleptic rankings by panels, a satisfactory relationship is observed. For example, Figure 7 shows this relationship for typical experiments in which mixed groups were presented for visual ranking. Data for a series of visual rankings of brown color formation for heating of dry whole egg powder are given in Table 5 together with statistical significance for these rankings and measured browning values.

3.4 Browning Tolerance of Fruits At Elevated Temperatures

3.4.1 Introduction

Studies on heat tolerance of fruit pieces were initiated in Phase III. These tests are identical in concept with heating studies conducted on nonfat milk and whole egg, which have been reported upon in earlier sections. The studies have been conducted on apple slices in the dry state and during freeze drying, and on osmotically pre-treated apples as well as apples of natural solids conentration. Similar studies were also conducted using osmotically treated (sucrose) cantaloupe.

3.4.2 Method for Quantifying Extent of Browning

Extraction procedures for quantifying the extent of browning were tested using either distilled water or 50% ethanol for extraction of the brown color. While the water solution could not be clarified, the 50% ethanol was clear after filtration, and the absorption spectra was determined over the range 400 to 600 nm. No absorption maximum was observed, but at about 500nm, a reasonable balance of separation of absorption values for different heating times and slope of the absorbance-wavelength curve was observed. This wavelength was therefore utilized.

The procedure is given below.

1) Exactly 2.0 g of crushed dried apple sample is weighed into a 50 ml erlenmeyer flask.

2) 20 ml of a 50% aqueous ethanol solution is added.

3) The sample is shaken for 1/2 hour at room temperature.

4) The sample is gravity filtered through #576 filter paper to yield a clear extract.

5) The optical density of the filtrate is read at 500 nm using a 50% ethanol solution as a blank.

6) The browning value is defined as $\frac{(OD_{500})\ (100)}{\text{Sample weight}}$

When samples, which had been heated for different times and temperatures, were evaluated for browning values, an acceptable correlation resulted. When this quantitative method was correlated with visual ranking studies (Table 6), there arose some questions as to the success in the measured values. The correlation seems somewhat poor and further, the ability of the panel to differentiate brown colors at a high level of statistical significance, with these samples having only slight differences in browning value, lends further weight to questioning the applicability of this extraction method for measuring browning.

3.4.3 Results of Browning of Fruits at High Temperatures

In one study freeze dried osmotically treated apple slices were heated at 80, 90 and 100°C for periods of up to 3 hours. The heated samples were then ranked according to

acceptability of color (limits of acceptability were 2 hours at 80°C, 1 hour at 90 or 100°C). These results have been presented in Table 7. A batch of "acceptable" sample (2 hours at 80°C) was then prepared for organoleptic evaluation of taste compared to unheated osmotically treated apples and untreated apples. Results, which are presented in Table 7, show that osmotically treated apples are rated higher than the untreated, and that no significant difference was noted between the heated and unheated osmotically treated apples.

In another experiment, this time using apple slices without pretreatment, the effect of freeze drying as single layers at heating plate temperatures of 80°, 100° and 120°C was investigated. Apple temperature reached as high at 110°C. There was little browning observed, except at 120°C, where it was noticeable, but not quite objectionable. The flavor of the heated apples was classified as "different, but acceptable" when compared to unheated freeze dried apples. It was characterized as tasting like cooked apples. The texture was slightly crisper than apples freeze dried without heating. Drying times were significantly reduced as the heating temperatures were increased, so that dry product throughput was increased without significant loss of product quality.

To further increase the throughput during drying, apple slices (no osmotic pretreatment) were freeze dried in beds approximately 3 slices (12-18 mm) thick. The table

below compares the data obtained for apples dried at heating plate temperatures of 100°C.

	Upper heater (°C)	Lower heater (°C)	Drying time	Wet feed throughput kg/m^2 hr	Browning
Single layer	100	100	3 1/2	0.74	none
Multilayer	100	100	8	1.01	slight browning, upper layer
Multilayer	80	100	7	0.96	no browning

It can be seen that an almost 33% increase in throughput can be obtained by freeze drying in layers without observable browning. The rates of throughput are quite acceptable when compared to "maximum sublimation rates" obtained by freeze drying slabs of ice at constant heater temperatures.

Osmotically treated cantaloupe samples which had been heated either during or after freeze drying (in the dry state) were evaluated by organoleptic rankings of taste quality. The results show that degradation of quality is more severe when samples are heated during freeze drying than when heated in the dry state (Table 8).

3.5 Analysis of freeze drying behavior

As a part of the studies on degradation of nutrients due to heating at high temperatures, browning of nonfat milk has been studied. To eventually incorporate this data into freeze drying studies, a method for analyzing the freeze drying behavior of foods is necessary. As a first step, a technique combining experimental and computer simulation data was developed. Interaction of freeze drying behavior and degradation kinetics has not, as yet, been evaluated by a single analytical computation technique, but should be achievable by use of information of the type developed in these studies.

Two research articles, which have been published in the Journal of Food Technology, are appended. One describes the methods used to develop simulations of freeze drying, while the other presents a method by which moisture profiles in the dry layer may be calculated on the basis of the easily measured temperature profiles.

J. Fd Technol. (1974) 9, 329–344.

A combined experiment-computer technique for determining heating programs for batch and continuous freeze dryers

J. M. AGUILERA* AND J. M. FLINK

Summary

Two parameters, which characterize the freeze drying process, are obtained by a linear regression of variables derived from data from a limited number of freeze drying experiments. Freeze drying times and sample temperature profiles can then be simulated for other processing conditions, using computer techniques. The simulation has been used to predict the drying behaviour of skim milk samples for a continuous freeze drying process. The results of the simulation agree closely with a batch freeze drying operated so as to model a continuous process.

Introduction

Production of freeze dried food products has shown such sizeable growth in the past few years, especially in the area of instant coffee, that the process must be considered as established on an industrial scale. Further growth of the process by application of freeze drying to products of lower inherent value requires close regulation of process parameters so that freeze dryer utilization is optimized.

The ability to rapidly determine this optimum would allow use of continuous freeze dryers for short production runs (days or weeks) of freshly harvested products or contract freeze drying. The economic savings by using continuous freeze dryers has been quoted to be 30–40% over batch type units (Anon., 1972). This type savings could further fuel the interest in freeze drying of foods. Flink & Fosbøl (1972) described a number of techniques by which optimal freeze dryer heating programs could be determined; however, most of these are difficult to implement at present. Thus, in practice, the technique used is a trial and error approach. As noted by Blair (1966), 'specifying an optimum processing cycle usually required many full scale production runs, each an improvement over the proceeding'.

The development of adequate mathematical techniques would greatly improve the situation over trial and error, for computer techniques could be applied to the mathematical formulations. A few studies have been reported for the air drying of beds of

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grain products. Bakker-Arkema, Evans & Farmer (1971) simulated the multizone drying of grain and were able to study the influence of a number of process variables on sample moisture contents and temperatures. Experimental measurements closely followed the computed values.

Two works have been reported in which physical parameters that are obtained during drying are used in the mathematical expressions for further simulation. Rowe & Gunkel (1972) used a diffusional model to evaluate thin film drying of forage. Application of suitable simplifying assumptions allowed calculation of a drying coefficient which was directly proportional to the moisture diffusivity. Other unknown parameters were determined by least square fits of normalized drying equations. The drying simulation was then obtained by simultaneous solution of mass and energy balances of the system. Husain *et al.* (1972) required simplification of the complex equations for simultaneous heat and mass transfer during the falling rate period in order to apply digital computer finite difference methods to the resulting differential equations. Experimental drying data were used to evaluate the parameters for use in theoretical drying solutions. Good agreement between experiment and theory were obtained only when certain parameters were divided so that different values applied to different stages of the drying.

Mathematical approaches to the modelling of freeze drying have been presented by a number of authors, though in most cases little consideration was made to utilization of these techniques to simulation problems. Two research groups have been particularly active in developing mathematical expressions for the freeze-drying process and associated physical behaviour. Both utilize the Uniformly Retreating Ice Front (URIF) model, in which a sharp boundary is postulated to exist between the ice and the dry layer. King (1971) has presented a review of arguments for and against this model. Tests on the applicability of the URIF model showed that it was usable only up to the removal of 65–90% of the initial water (Sandall, King & Wilke, 1967) and that other difficulties related to product nonuniformity and piece size (edge effects) are possible (Margaritis & King, 1971).

In a series of literature reports, mathematical expressions have been developed for the analysis of freeze drying under various processing conditions (Dyer & Sunderland, 1967, 1968, 1971; Cho & Sunderland, 1970; Massey & Sunderland, 1972). They showed that by treating freeze drying as a quasi-steady state process the mathematical expressions could be sufficiently simplified to allow computer solutions. Through this, it was shown that convection heat transfer was negligible. For radiation heat transfer, relationships developed between radiator temperature, sample surface temperature and ice front temperature showed a two phase temperature behaviour of constant heater/variable surface followed by variable heater/constant surface. Meo & Friedly (1973) have shown this to be a condition for optimal control of freeze dryers.

Heldman & Hohner (1972) simulated mathematically the atmospheric freeze drying of beef cubes. Simplifications of the complex equations (heat and mass transfer balances)

were evaluated by numerical analysis techniques using the digital computer. Using values of product properties from the literature, they obtained acceptable results.

Flink & Fosbøl (1972) noted that mathematical approaches to simulation of freeze drying could be based on (1) complex equations with independent determinations of the various parameters or (2) simplified equations with lumped parameter determination obtained from experiment. Each has positive and negative factors, relative to speed, convenience, accuracy, etc. For developing practical heating programmes for continuous freeze drying of a particular product, we feel that the second method will be more successful.

This paper discusses the development of (1) simplified drying equations having grouped mathematical constants which are the parameters of drying; (2) obtaining of these parameters by means of a few simple experiments; (3) computer simulations of drying (batch and continuous) using the experimentally measured parameters.

Methods

Experimental

Reconstituted nonfat dry milk powder (20% w/w) with added sodium carboxymethyl cellulose (0·5%) (Dupont Chemical Co.) was used for freeze drying. An Avicel, dextrose, CMC model system was also successfully used, but will not be reported upon here (see Aguilera, 1973). After mixing, the sample was poured into an aluminium pan which was fitted with seven fine-wire thermocouples at known locations and a rubber ring on the circumference to prevent edge effects during drying (Fig. 1). Freezing was conducted by placing the sample holder on a thick aluminium plate which was immersed to a known depth in liquid nitrogen. In this way reproducible and controlled rates of freezing could be obtained. The sample was completely frozen in 1 hr. Prior to placing in the freeze dryer, the internal temperature gradients were allowed to equilibrate by holding the sample in a styrofoam support. The equilibrated frozen sample in its styrofoam holder (now used to insure one-sided heat transfer) is placed in the freeze dryer. The freeze dryer is quickly evacuated and then the heating plates are activated (come-up times of less than 5 min). The energy input to the heating plates is controlled by a thermocouple type controller which can use measurements at the heating plate or various sample locations as inputs. In these experiments, control was based on either the heater plate or sample surface thermocouples. The sample and system temperatures were measured each 6 min with a 12 point recorder. Additionally, instantaneous readings of selected locations could be made using an electronic thermometer. Chamber pressures were monitored using both Alphatron and thermocouple gauges. The sample was supported in the drying chamber on a Mettler balance, so that continuous weight measurements could be made.

The drying procedure involved utilization of a constant heater temperature until the surface reached a particular temperature value called the 'scorch' temperature; that

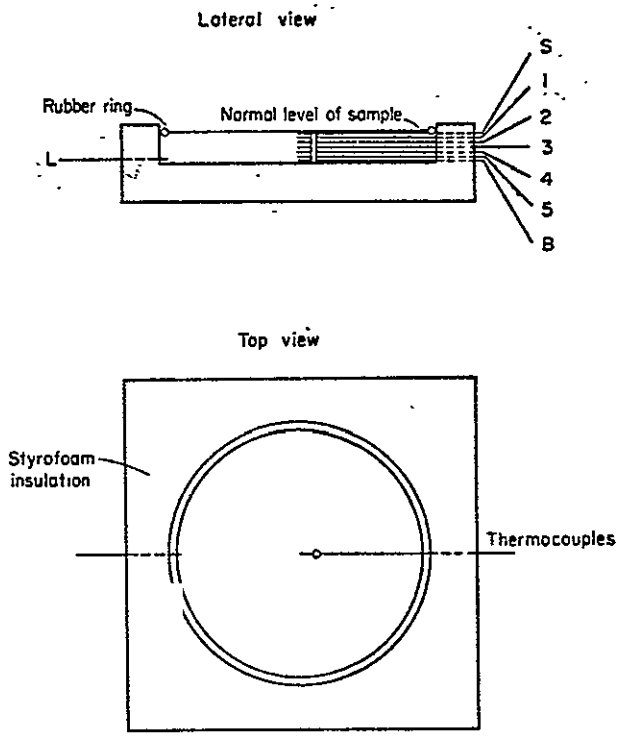

FIG. 1. Schematic of sample holder (to scale).

is, the maximum allowable temperature for retention of product quality. At this point the controller was switched to the sample surface, which was then maintained at the scorch temperature. For these experiments, a scorch temperature of 56°C was arbitrarily chosen.

The end point of drying was designated as the time when the temperature difference between the surface and bottom thermocouples was less than 6°C. Following drying, moisture contents of the dried material were measured gravimetrically using vacuum oven heating of 24 hr at 70°C. The thermocouple tips were carefully exposed and their location measured with a cathetometer.

Parameter determination

Relationships between various freeze drying variables were obtained based on the model used by Cho & Sunderland (1970), a semi-infinite slab dried by radiation from one side. Equations involving a single parameter were developed for heat transfer from the radiator to the ice interface of the sample

$$r = \Omega \frac{T_S - T_I}{T_H^4 - T_S^4}$$

and for conduction heat transfer through the dry layer supplying the energy for sublimation,

$$T_S - T_I = \phi r \frac{dr}{dt}.$$

Thus, the parameter Ω relates external and internal heat transfer, while ϕ relates internal heat transfer with energy consumption. Neither parameter has been restricted as to its functional dependence on other system factors.

The data obtained by the experiments were analysed by digital computer using a polynomial regression subroutine. The main steps of this program are presented in Fig. 2. The maximum degree of the polynomial was chosen to be one for the determinations of Ω and ϕ, because of a desire to have a linear relationship. A cubic equation was developed for interface position v. time, based on times at which thermocouple readings raised from the ice front temperature. The first derivative of this equation

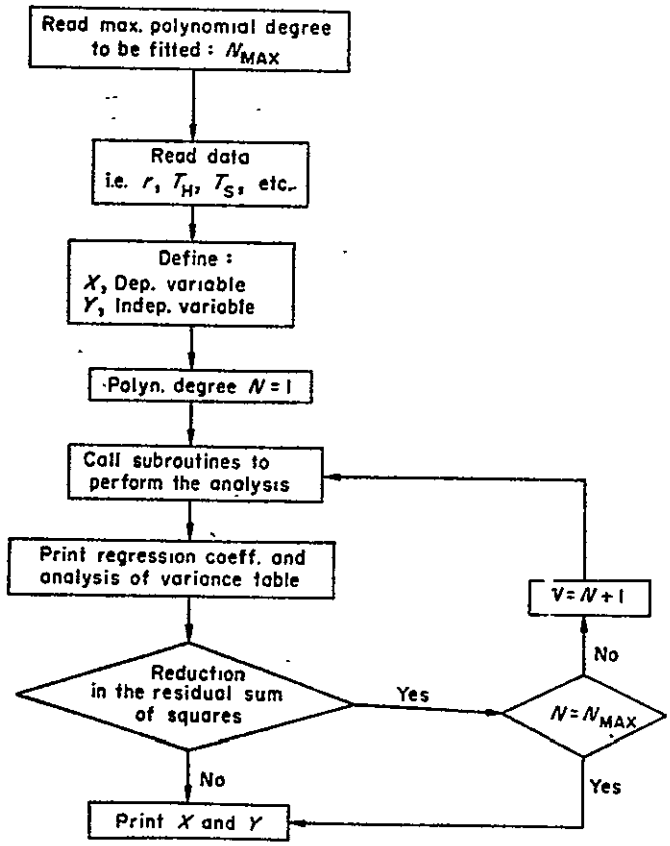

FIG. 2. Flow diagram of the computer program for parameter determination.

gave the value of dr/dt. This is then used in the determination of ϕ. Referring again to the programme flow diagram (Fig. 2) the following were the x and y variables:

	Variable	
Parameter	x	y
Ω	$\frac{T_S - T_I}{T_H^4 - T_S^4}$	r
ϕ	$r\frac{dr}{dt}$	$T_S - T_I$

Drying simulation

The basic equations presented above are coupled to appropriate boundary conditions and solved simultaneously to give drying temperatures and interface positions as a function of time. The major steps of this process are shown in Fig. 3. The calculation considers the time necessary to get the interface to the sample bottom (disappearance of ice). The equation including the Ω factor will give the surface temperature, while the ϕ containing equation gives the time to reach various interface locations.

Results

Initial experiments showed that the ice front was quite sharp and uniformly retreating into the sample. Also, the sample underwent some cracking during the drying process. The cracks were quite small and uniformly distributed.

Duplicate freeze drying experiments which were conducted at heater temperatures of 78, 100 and 128°C gave good reproducibility. Typical results are presented for a drying at 128°C (Fig. 4) in which the scorch temperature (56°C) is reached after about 3½ hr. The linearity of the temperature profiles in the dry layer (Fig. 5) shows that the quasi-steady state approach is applicable. The curves lose their linearity when the ice layer disappears. The constant ice temperature value observed allows the use of the mentioned equations. Measurements of the final moisture content at three locations showed no radial distribution of moisture. At the end of sublimation, moisture contents varied from 12–32 g H_2O/100 g solids, while at the end of drying the moisture contents were below 1 g H_2O/100 g solids.

The parameters were obtained by fitting a straight line to the data. Fig. 6 shows that excellent correlation was obtained for Ω giving values of 0·659, 0·648 and $0{\cdot}617 \times 10^8$ for 78,100 and 128°C respectively. For simulation purposes a mean value of $0{\cdot}640 \times 10^8$ °K^3 was used.

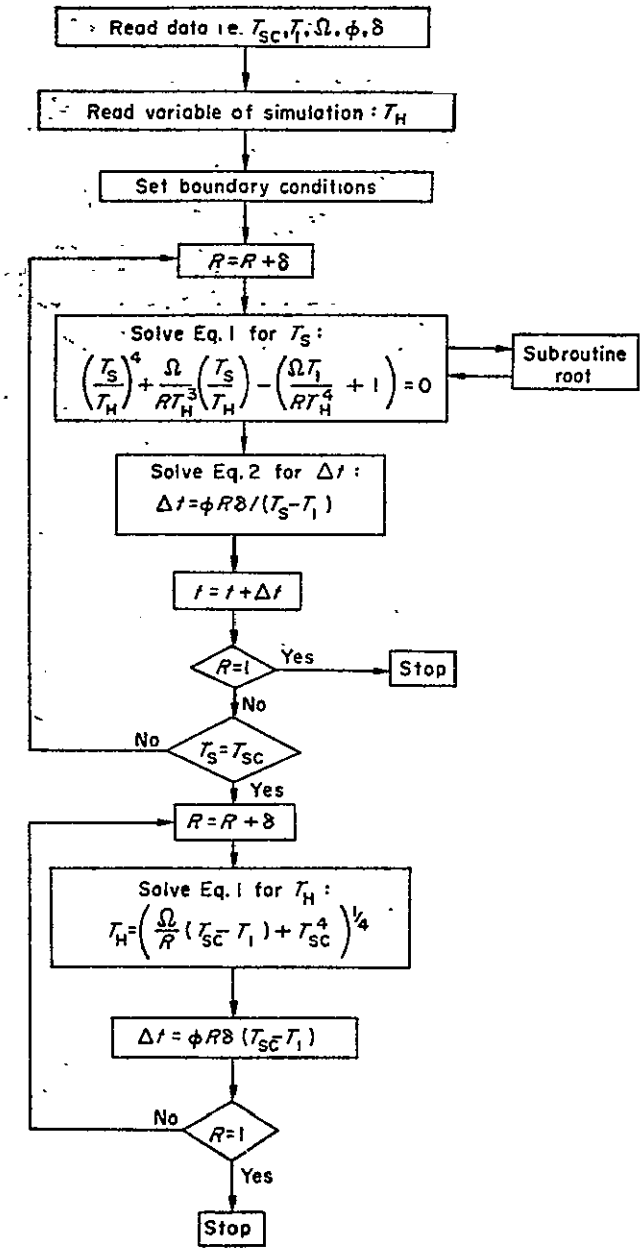

FIG. 3. Flow diagram of the computer program for freeze drying simulation.

For the ϕ parameter determination (Fig. 7) a straight line fit of all data was satisfactory only for a heater temperature of 78°C, where the entire sublimation process occurs without the surface reaching scorch conditions. In the other two cases, 100 and 128°C, two clearly distinctive zones, one before reaching scorch temperature and the

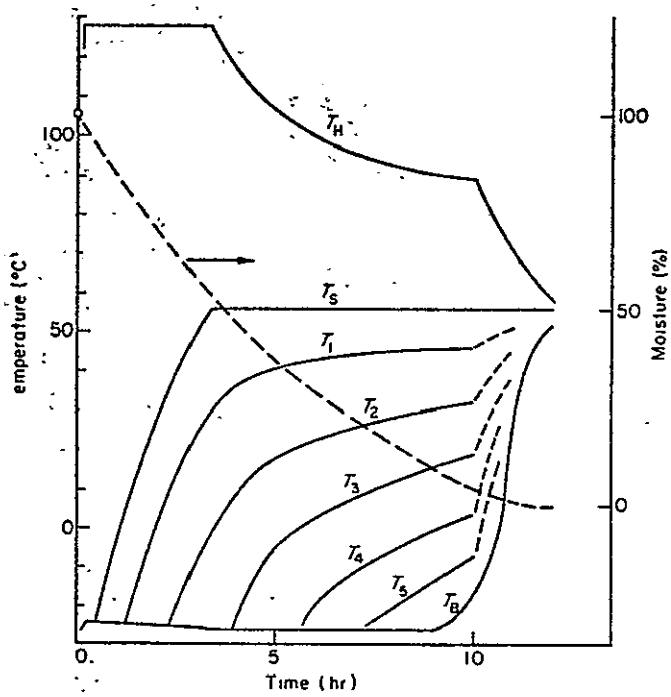

FIG. 4. Sample temperatures at seven locations and sample moisture loss when freeze drying skim milk. Initial heater temperature = 128°C; scorch temperature = 56°C.

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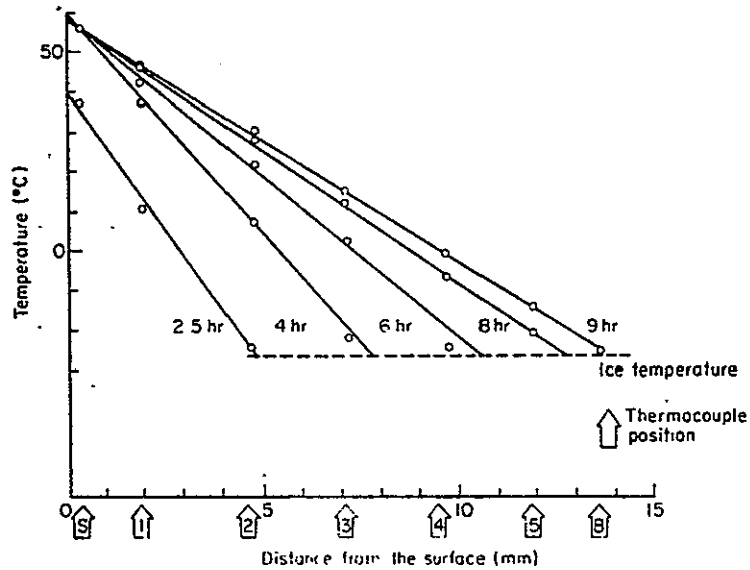

FIG. 5. Temperature profiles in freeze drying skim milk when the initial heater temperature is 128°C and the scorch temperature is 56°C.

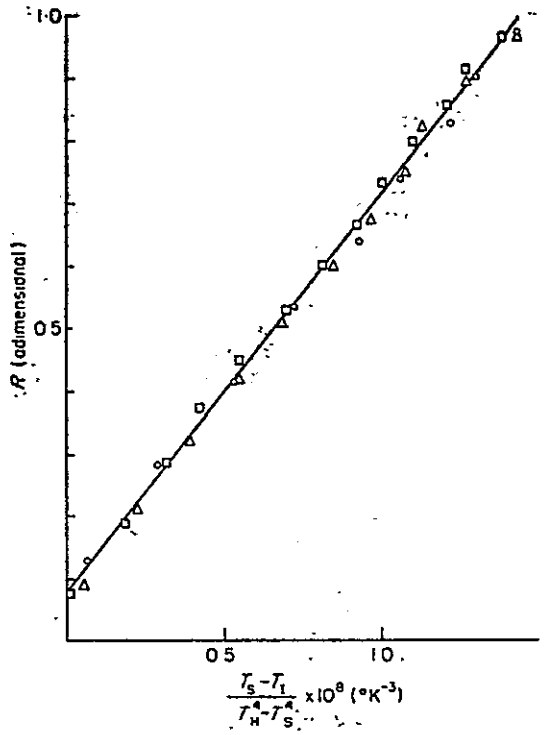

FIG. 6. Redefinition and replotting of temperature and moisture data for determination of Ω parameter. T_H(°C): □, 78; △, 100; ○, 128.

other after, were observed. The value of the slope of the least squares straight line fitting all data at each temperature was defined as ϕ mean ($\bar{\phi}$) for that temperature. Values of ϕ for the initial time (prior to attaining the scorch temperature) and for the entire process are shown in Fig. 7 for a 100°C heater temperature.

Considering the data further shows the following facts.

(1) The value of the slope of the imaginary straight line that fits the data prior to attaining the scorch temperature ($\bar{\phi}^{initial}$) represents the ϕ value for a given heater temperature with the following relation being observed:

$$\bar{\phi}^{initial}_{128} > \bar{\phi}^{initial}_{100} > \bar{\phi}^{initial}_{78}$$

(2) After attaining the scorch temperature, the temperature of the heater will be reduced. Another evaluation method for ϕ could take this into account by lowering ϕ with heater temperature (Fig. 8). It would also be possible to find a function that correlated the reduction in ϕ with the interface position.

The parameters Ω and ϕ, obtained as described above, are used in the computer simulation programme to calculate freeze drying behaviour of skim milk samples. Table 1 gives results of experiments and various simulations for three initial heater

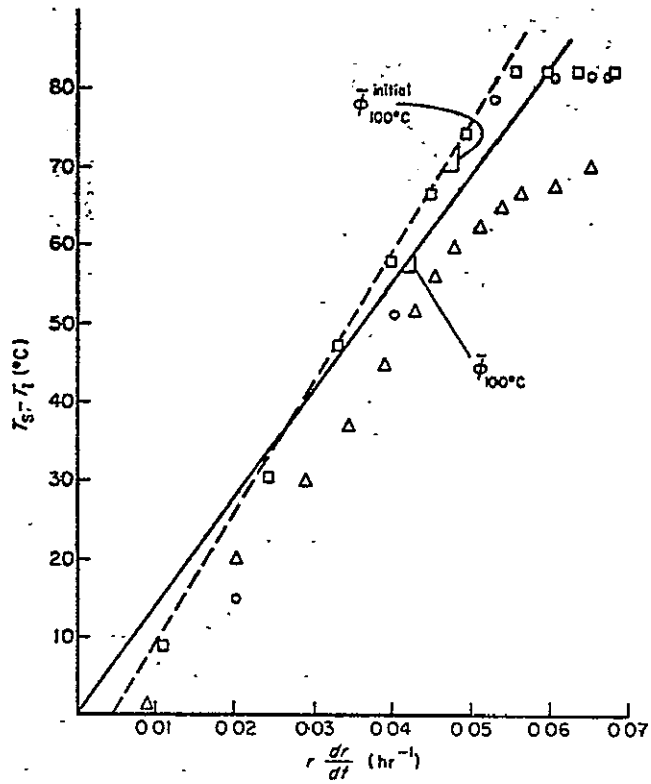

FIG. 7. Redefinition and replotting of experimental data for determination of ϕ parameters (see text). T_H(°C): △, 78; □, 100; ○, 128.

temperatures. For the purposes of simulation, freeze drying can be divided into four periods: (1) an initial lag or equilibration period, (2) a period before the sample surface reaches the scorch temperature (period or stage I), (3) a period where the surface is at the scorch temperature but ice is still present in the sample (period or stage II) and (4) the desorption period. It was observed that equilibration took approximately 20 min, and desorption about 2 hr, independent of initial heater temperature. In the case of desorption, this occurs since the initial desorption conditions (sample surface at the scorch temperature and sample bottom at the ice front temperature) give an identical temperature gradient in all cases. Table 1 gives times to reach the scorch temperature, and the total time to achieve disappearance of the ice. For each heater temperature two basic types of results are presented: (1) results of duplicate freeze drying experiments and (2) results of simulations based on the derived parameters. Since the values of the Ω parameter were independent of heater temperature, the average Ω value was used in all simulations. The variation of the ϕ parameter necessitated simulations according to three approaches, (1) self-simulation in which ϕ values for a given heater temperature are used to calculate the drying behaviour for that

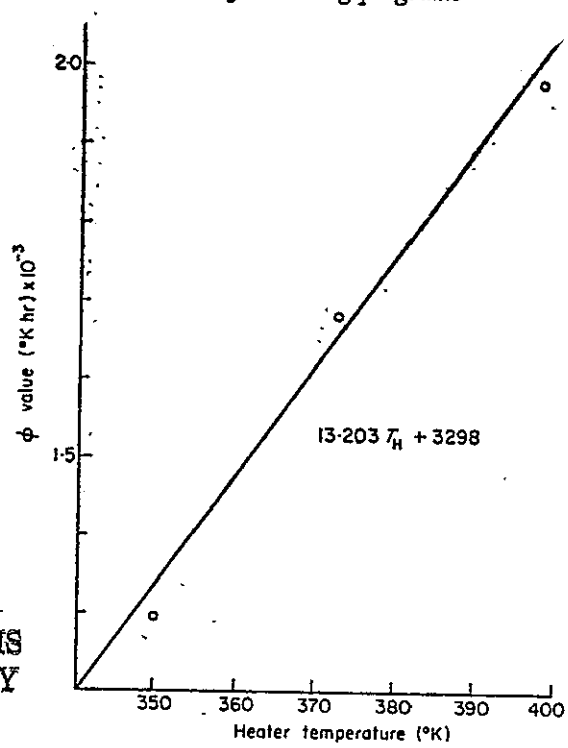

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FIG. 8. Variation of ϕ parameter with heater temperature.

heater temperature, (2) cross-simulation in which ϕ values at other heater temperatures are used and (3) the case where $\phi = F(T_H)$ is used for the simulation. (Thus for example, in Table 1, for a heater temperature of 78°C, the data source *Experiment* gives the observed results, $\bar{\phi}_{78}$ gives a simulation using the ϕ obtained from a 78°C experiment, $\bar{\phi}_{100}$ and $\bar{\phi}_{128}$ gives simulations of drying at 78°C using $\bar{\phi}$ values obtained from 100 and 128°C experiments and $\phi(T_H)$ gives simulation using ϕ values as a function of calculated heater temperature.)

At a heater temperature of 78°C all predictions were below the experimental value from 5 to 50 min. The fact that $\bar{\phi}_{78}$ gave the poorest simulation could indicate that tailing effects at the end of drying, especially when the scorch temperature is not reached, could be of importance. Simulated surface temperatures at the end of sublimation were in excellent agreement with the 46°C value obtained in the experiment; differences were less than 2°C.

At a heater temperature of 100°C, predicted times were again less than the experimental value. For constant $\bar{\phi}$ simulations the best prediction corresponded to the self simulation ($\bar{\phi}_{100}$). Sizeable improvements were obtained with the use of ϕ (T_H) which predicted times within 30 min of the experimental time for periods I and for the total drying time. Again, final heater temperatures were in excellent agreement with the experiment; differences varied less than 1·5°C.

TABLE 1. Experiment and computer simulations of batch freeze drying of skim milk

Heater temp.	Data source	Time in Stage I	Interface position Stage I	Surface temp Stage I	Heater temp Stage II	Time in Stage II	Total time
78°C	Experiment	13 : 25		46·0			13 : 25*
	$\bar{\phi}_{78}$	12 : 35		46·2			12 : 35
	$\bar{\phi}_{100}$	13 : 20		46·6			13 : 20
	$\bar{\phi}_{128}$	12 : 50		47·7			12 : 50
	ϕ_{TH}	12 : 50		46·9			12 : 50
100°C	Experiment	7 : 40	0·73	56·0†	88·0	3 : 45	11 : 30
	$\bar{\phi}_{78}$	6 : 00	0·70	56·0	88·4	4 : 00	10 : 00
	$\bar{\phi}_{100}$	6 : 10	0·69	56·0	87·9	4 : 30	10 : 40
	$\bar{\phi}_{128}$	5 : 30	0·65	56·0	86·6	4 : 50	10 : 20
	ϕ_{TH}	7 : 10	0·69	56·0	88·0	4 : 50	12 : 00
128°C	Experiment	3 : 20	0·45	56·0†	88·2	6 : 15	9 : 35
	$\bar{\phi}_{78}$	2 : 10	0·38	56·0	88·9	6 : 45	8 : 55
	$\bar{\phi}_{100}$	2 : 15	0·37	56·0	88·1	7 : 15	9 : 30
	$\bar{\phi}_{128}$	2 : 05	0·36	56·0	87·0	7 : 15	9 : 20
	ϕ_{TH}	3 : 10	0·38	56·0	88·0	8 : 20	11 : 30

$\bar{\phi}_{78}=1294\cdot3$; $\bar{\phi}_{100}=1387\cdot1$; $\bar{\phi}_{128}=1365\cdot5$; $\phi_{TH}=13202_{TH}+3298$.

* No stage II present, so total time is equal to time in stage I.

† By definition, at end of stage I $T_s=56$°C.

At a heater temperature of 128°C errors of more than 1 hr in period I times, using constant ϕ, were greatly reduced when $\phi=F(T_H)$ was used. However, the total times were overestimated by almost 2 hr while good results were obtained with mean ϕ values.

In summary, mean values of ϕ tend to produce slight underestimation in total times and sizeable underestimation in period I times. On the other hand, the relation $\phi=F(T_H)$ was extremely precise in the determination of period I times, but underestimated total times at low heater temperatures and overestimated them at high heater temperature.

Basically, the theory and numerical simulation methods for continuous freeze drying are the same as those for the batch process. In continuous freeze drying, it is not a single heater temperature that characterizes the process, but the existence of several 'zones', each at a particular constant heater temperature, and where the product resides for fixed (usually equal) periods of time.

Thus, the simulation of a continuous freeze drying can be performed with the same programme as developed for batch processes. The two parameters, temperature and time can be manipulated so as to calculate minimum total drying time with acceptable sample temperatures.

In this case, however, to evaluate the potentialities of the method a predetermined three-zone heater programme was used to dry a skim milk sample and then the same experiment was simulated in the computer using Ω and ϕ values from the batch experiments. Results, presented in Fig. 9, show the good agreement between experiment and simulation.

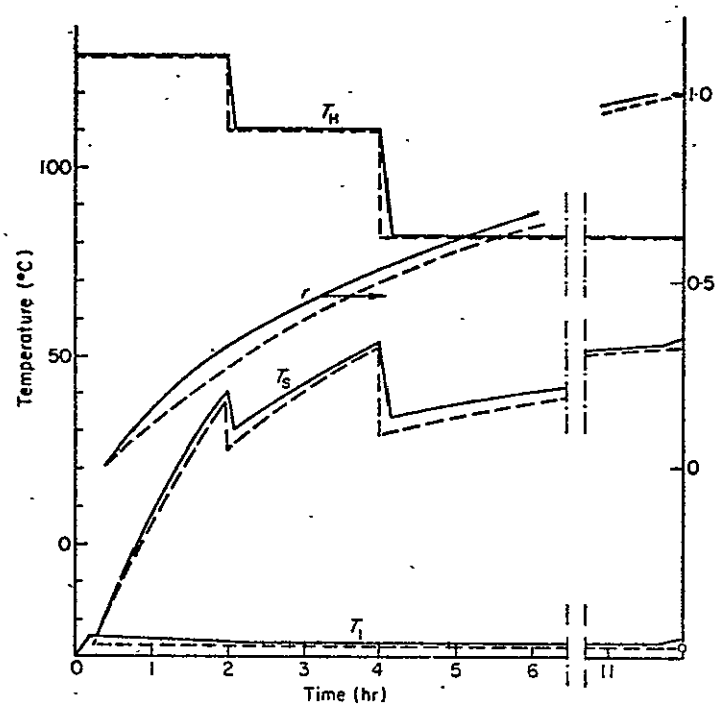

FIG. 9. A comparison of experiment with computer prediction for a simulated continuous freeze drying process (see text). ——, Experimental; – – –, simulation.

Discussion

The determination of drying parameters was made under a self-imposed constraint of simplicity; meaning in this case, the desirability of linear relationships between variables so that the slope of the straight line is numerically equal to the drying parameter.

The Ω parameter gave the desired behaviour in all cases. A general trend, noted by Aguilera (1973) shows that the linear relationship holds for various levels of heat transfer efficiency, the slope changing (i.e. Ω changing) to give revised drying times. The accuracy of the Ω parameter is reflected in the excellent agreement between experimental and calculated temperatures.

Since from simple theory Ω represents $k/e\sigma$, values of thermal conductivity can be calculated from Ω values, if a combined dryer efficiency (geometry) and heater emmisivity is equal numerically to the emissivity of the sample and is taken as 0·8 (used by

Gentzler & Schmidt, 1972). Calculated values of k vary from 0·0340 to 0·0354 kcal/m hr °K comparing well with recent values reported by Gentzler & Schmidt (1972) for freeze-dried evaporated skim milk (0·0450 kcal/m hr °K for transient determinations and 0·024 kcal/m hr °K for steady state methods).

With respect to the ϕ parameter, which is directly responsible for the time determination, some special factors which reduce the accuracy must be noted. The ϕ parameter is associated with the distribution of heat inside the sample. It is well known that there exist several sinks for heat conducted through the dried layer, the principal one being the sublimation of ice. As drying proceeds the relative importance of other heat sinks, especially the desorption of water, tend to increase as monolayer moisture values are reached. Thus, it is not surprising to find a tailing effect in the plot for ϕ determination (Fig. 7) in experiments where nonscorch conditions prevail over the entire sublimation period (such as 78°C). Another source of inaccuracy of the ϕ parameter is that ϕ is doubly dependent on the interface position ($r\,dr/dt$) whose accurate measurement is difficult due to both theoretical considerations and experimental difficulties.

The theoretical type considerations deal primarily with definition of the interface and its measurement. It has been postulated here that the interface passes a particular location (a thermocouple tip) when the temperature starts to rise above the ice front temperature. From the practical view point, the response time for descernible rise of the temperature places a degree of uncertainty on the time. Interface location can also be measured by weight loss, but here dry layer desorption will show some influence on presumed interface location.

The experimental difficulty which influences ϕ parameter determination relates to sample holder design giving a slightly uneven interface. While it has been demonstrated that the freeze drying is quasi-steady state (Fig. 5), with a constant ice front temperature (Fig. 4), the presence of a planar ice front was true for only a part of the process. Comparison of moisture loss (by weight measurements) with interface position (by thermocouple measurements) showed uniform drying for 2/3 of the thickness, followed by a nonuniform period. This difficulty is probably related to heat conduction in the sides and bottom of the sample holder. Thus an improved sample holder and definition of interface location will lead to improved values of ϕ.

In the practical case, the ϕ values obtained allowed simulation of the drying times. The small errors involved in self simulation are explicable by the use of average ϕ values, although in no case does the difference between calculated and experimental time exceed 50 min or an error of 8·0%.

Cross-simulation using average ϕ values was successful in predicting total times, but less accurate for period I times. This was due to the fact that the actual slopes in the ϕ determination plots were steeper in the first part of drying than the calculated mean value.

The slight refinements of the relationship between drying parameters (in this case ϕ)

and the measured drying variables (in this case T_H) gives a sizeable improvement in the subsequent computer drying simulations. Thus, the use of the linear function $\phi = F(T_H)$ enchanced the simulation of the period I times.

Conclusions

Computer simulations of freeze drying behaviour can be produced using simple equations and experimentally determined parameters for these drying equations. A minimum of three batch freeze drying experiments are necessary to obtain the linear relationship of the ϕ parameter.

The computer simulation has been used to predict the drying behaviour of a skim milk sample under conditions present in continuous freeze dryers, with very close agreement with experiment.

The technique of computer simulation will allow optimization of continuous freeze drying processes. In particular, it should be possible to contemplate achieving the improved economies of large continuous freeze dryers for small production runs of seasonable products, or for contract freeze drying by means of three rapid small batch freeze dryings (for parameter determination) followed by the computer simulation and optimization for the continuous freeze drying for production.

Acknowledgment

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Appendix

Symbol	Description	Units
k	Thermal conductivity	kcal/hr m °C
r	Interface position	Adimensional
t	Time	hr
T	Temperature	°K
ϵ	Emissivity	
σ	Stefan-Boltzmann constant	kcal/m² hr °K⁴
ρ	Density	g/cm³
ΔH	Heat of sublimation	kcal/kg
Ω, ϕ	Freeze drying parameters	

Subscript	Refers to
H	Heater
S	Surface
I	Ice
1, 2, 3, 4, 5	Thermocouple position
sc	Scorch conditions

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Technical note: Determination of moisture profiles from temperature measurements during freeze drying

JOSE M. AGUILERA AND JAMES M. FLINK

Introduction

It has been shown that computerized simulation of freeze drying can be used to predict product temperatures and moisture contents (or water activities) as a function of time and geometric location (Aguilera, 1973; Aguilera & Flink, 1974). Since destruction rates of various important nutrients (as well as activation energies) are a function of temperature and moisture content, knowledge of temperature and moisture profiles inside a piece of food during processing is extremely important for predicting the extent of quality deterioration for particular process conditions. This is necessary for determining optimal processing policies (Labuza, 1972). In work done in our laboratories, literature data for non-enzymatic browning of potato dices was combined with computer-simulated product temperatures and moisture profiles corresponding to common commercial conditions. The results, which gave the distribution of brown colour, demonstrated the value of this type of technique to better define quality changes in processing (Aguilera & Chirife, 1973).

For freeze drying, many examples of temperature profiles are available from the literature. Contrary to this is the limited number of moisture content profiles available. Meffert (1965) determined moisture contents in layers of swede, finding basically the characteristic two zone phenomena, dried layer and ice core. Also, clearly distinguishable was the existence of a moisture gradient through the dried layer that varied from around 3·0 g H_2O/100 g solids near the outer surface to 33·0 g H_2O/100 g solids near the interface when the ice core had receded half-way into a 3·6 cm sample dried from both sides. In addition to the two above mentioned zones, Bralsford (1967) postulated the existence of a transition zone between them, which he labelled the 'diffusion zone'. He felt that at higher chamber pressures, appreciable quantities of liquid water were present in the ice core so that some liquid diffusion into the dried layer resulted. Broadening of this zone was postulated to be due to solute migration in which more and more ice melted as the zone receded into the ice core. In support of this hypothesis, he presented the fact that at the very end of sublimation, samples that were removed and cut open presented a soft wet area, while those sectioned at the beginning of the process had a quite solid ice core.

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Hatcher, Lyons & Sunderland (1971) measured moisture distributions in beef samples with a gamma ray attenuation technique. Their measurements showed that there was almost a complete removal of moisture in the dry layer after the passage of the phase change region meaning that any transition zone was thinner than the sensitivity of their technique ($\simeq$5 mm). Almost linear temperature gradients were found in the dried layer during sublimation. Similar temperature profiles in beef were obtained by Brajnikov *et al.* (1969), but with respect to moisture they postulated the existence of a 'zone of sublimation'.

Recently, based on the higher desorption temperatures for bound water as compared with the sublimation temperature for frozen water, Gentzler & Schmidt (1973) postulated a relationship between bound water content (W_B) and temperature difference (ΔT_B) between any position in the dry layer (desorption temperature) and the temperature of the ice (sublimation temperature) that can be expressed mathematically as

$$W_B = e^{(a\Delta T_B + b)} \tag{1}$$

with a and b as constants dependent on each particular product. Gentzler & Schmidt (1973) presented data for skim milk. The same type of relationship can be obtained from data by Oetjen (1973) who worked with granulated coffee of 45% solids content (Fig. 1).

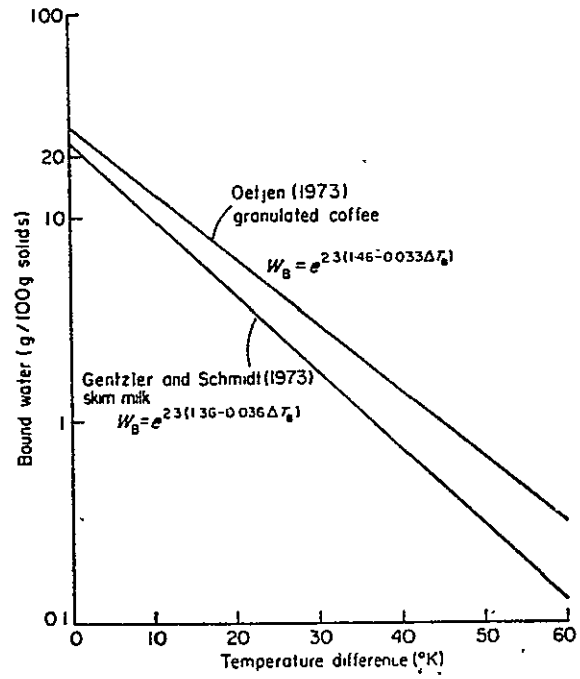

FIG. 1. Local moisture contents in the dry layer during freeze drying as a function difference of local temperature and ice front temperature.

The work reported upon here was undertaken to demonstrate the possibility of combining the bound water content and temperature difference data of Gentzler & Schmidt (1973) with dry layer temperature profiles obtained during freeze drying (Aguilera & Flink, 1974) to yield moisture profiles in the dry layer at various times in the drying process. These calculated moisture contents could then be included with temperature data in an integrated calculation of product deterioration using the temperature and moisture dependent kinetics of the degradative reactions.

Experimental

Samples consisted of a mixture of 20% non-fat dried milk, 0·5% sodium CMC and 79·5% water. The sample holder was a circular aluminum pan of 21·2 cm diameter provided with seven 30 gauge copper-constantan thermocouples. The sample thickness was about 14 mm. A 12 point temperature recorder continuously registered the temperature at those locations. After being frozen with liquid N_2, the sample was placed in a styrofoam-insulated support and placed in a pilot plant-size freeze drier. The heat input was initially controlled by a heater plate thermocouple in order to maintain constant heater temperature. When the surface thermocouple reached the maximum allowable product temperature, control of the heat input was switched to the sample surface thermocouple. Following freeze drying, determinations were made of moisture content, sample thickness and thermocouple positions.

Results and discussion

Temperature gradients in the dry layer for a heater temperature of 128°C are presented in Fig. 2. Important to note is the constancy of the ice temperature (T_I) and the linearity of the temperature gradient throughout the sublimation process. By recording the surface temperature (T_S) and following the interface position (r) by thermocouple measurements, the temperature at any point (x) in the dried layer can be easily determined using the relation:

$$T_x = T_S - \frac{x}{r}(T_S - T_I). \qquad (2)$$

Another interesting fact is the 'rotation' of the gradient that occurs about the constant surface temperature point, producing decreasing values for the temperature gradient as drying proceeds. Since the moisture content remaining after the passage of the ice front is directly related to the difference between local temperature and the ice front temperature as described previously, higher moisture contents are to be expected at a given distance from the ice front as drying proceeds. This is illustrated in Fig. 3 by combining equation (1) for the case of skim milk (Fig. 1) and the temperature gradients of Fig. 2. An explanation for the observations by Bralsford (1967) and Brajnikov *et al.*

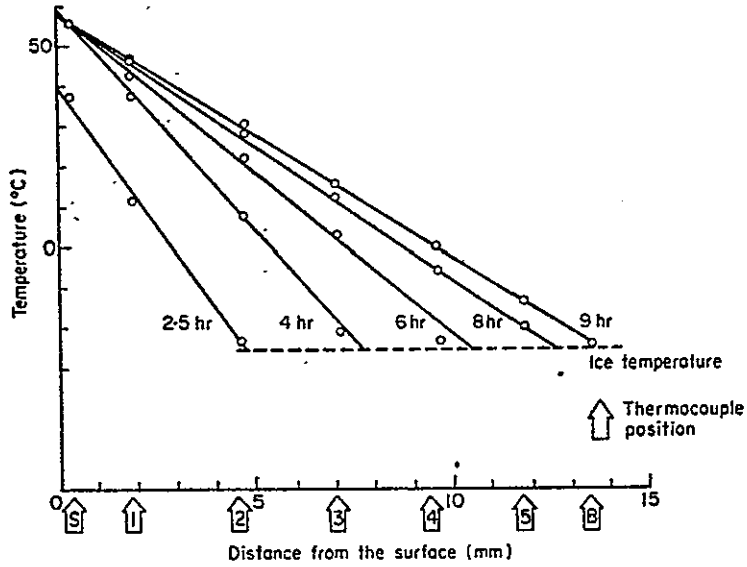

FIG. 2. Dry layer temperature gradients during sublimation period of freeze drying of skim milk (heater temperature = 128°C).

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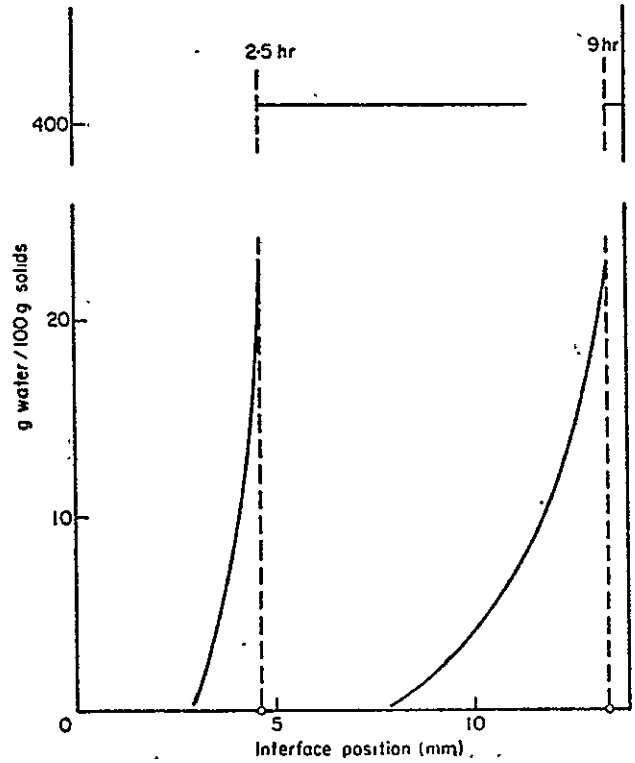

FIG. 3. Predicted moisture profiles during freeze drying of skim milk (heater temperature = 128°C).

(1969) of a soft wet broadening zone between the ice zone and the dried layer is obtainable from Fig. 3 since intermediate levels of moisture build up continuously against the ice front.

The present method, by developing moisture profiles, incorporates an important factor for optimization policies for quality retention in freeze drying. Our previous work (Aguilera & Flink, 1974) had considered only temperature effects on drying behaviour. Since quasi-steady state conditions prevail during freeze drying, a simple computer solution can combine temperature and moisture content dependencies during drying with kinetic data on product deterioration to determine a temperature-time heating program which minimizes deteriorative changes.

Conditions for quality retention are normally presented in terms of the maximum allowable product temperature (commonly called scorch temperature) which is usually considered to have a constant value. Actually, the degree of product degradation will depend on temperature, moisture content and time; hence, the 'scorch temperature', which may be defined as the temperature at which certain observable deteriorative processes acquire a predetermined critical value, will be a function of moisture content and time. Work with skim milk (to be reported later) shows the influences of moisture content (as well as temperature and time) and thus the need for developing sample moisture profiles.

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TABLE 1

Browning of Nonfat Dry Milk When Freeze Dried
With Heating Platens at 100°C

(Product surface generally reaches 100°C in 4 hours)

Browning Values

Time in Dryer	Whole Sample	Top	Middle	Bottom	Average of Layers
Sliced following drying					
4	9.4	7.4	6.7	5.7	6.6
7	20.5	30.6	18.4	12.8	20.6
Layered before drying					
4	7.7	6.0	5.0	5.6	5.5
7	12.4	35.0	10.0	13.4	22.8

TABLE 2

Acceptability of Freeze Dried Milk Samples

Visual Rank	Plate Temperature	Time	Browning Value[a]	Percentage Samples judged Acceptable
		Ranking Test 1		
1	100	1	2.8	100
2	100	1.5	3.0	100
3	Room Temperature	--	3.0	93
4	100	2	3.9	53
5	Spray Dried	--	3.7	0
		Ranking Test 2		
1	Room Temperature	--	2.0	93
2	100	1	2.8	93
3	120	1	2.4	71
4	100	2	3.9	71
5	120	1.5	5.6	36
6	120	2	15	14

[a] $\frac{(OD_{420})(100)}{\text{gm dry milk}}$

TABLE 3

Drying Rates and Browning for Freeze Dried Nonfat Milk

Sample thickness (mm)	Solids Content (%)	Heating plate temperature (°C)	Drying[a] rate kg/hr m^2	Solids[b] throughput kg/hr m^2	Browning Value[c]
12	20	80	1.29	0.30	2.39
12	20	90	1.26	0.33	2.44
12	20	100	1.41	0.32	2.52
12	20	110	1.43	0.32	3.32
12	20	120	1.75	0.41	3.75
12	20	130	1.75	0.38	3.22
12	10	100	1.14	0.11	1.99
12	20	100	1.41	0.32	2.52
12	30	100	1.71	0.51	2.94
6	20	100	1.36	0.27	2.15
6	20	110	1.32	0.26	2.35
6	20	120	1.29	0.26	4.65

a $\frac{\text{initial sample weight}}{(\text{drying time})\ (\text{tray surface area})}$

b $\frac{\text{weight of solids produced}}{(\text{drying time})\ (\text{tray surface area})}$

c $\frac{(OD_{420})(100)}{\text{gm dry milk}}$

TABLE 4

Some Properties of Heated Freeze Dried Milk When Rehydrated

Sample (RH/hrs @ 90°C)	Visual Evaluation of Color of Rehydrated Milk		Browning Value[a]	Solubility[b]
	Ranking	% of Time Acceptable		
0/0	1	100	1.3	2
0/2	2	90	1.2	2
0/3	3	90	1.5	4
0/6	4	80	1.9	6
0/4	5	60	1.8	5
11/2	6	10	1.9	5
11/3	7	10	2.1	6
11/4	8	0	3.2	7
11/6	9	0	4.0	7

a

$$\frac{(OD_{420})\ (100)}{\text{gm dry milk}}$$

b

1 = Soluble as instant spray dried

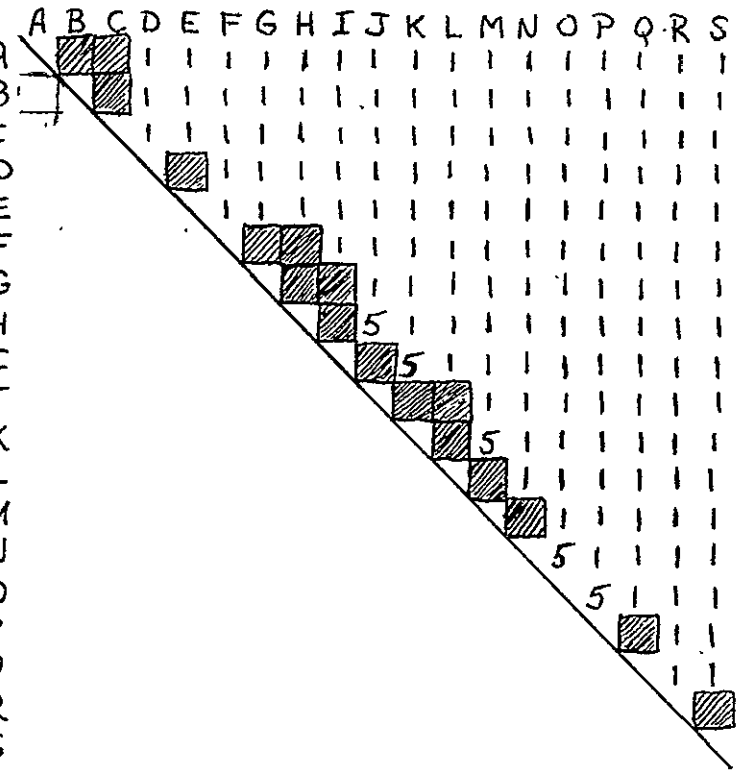
10 = Slightly soluble

Table 5

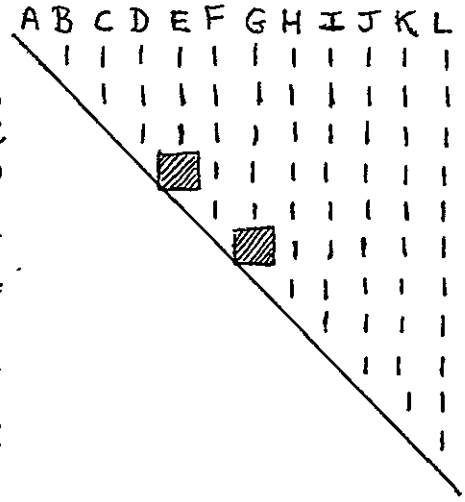
Browning of Dry Whole Egg: Visual Rankings according to Increasing Brown Color and Browning Values of Chloroform Extracts

A. SAMPLES HEATED AT 100 AND 110°C
B. SAMPLES HEATED AT 90 AND 110°C
C. SAMPLES HEATED AT 90 AND 100°C
D. SAMPLES HEATED AT 80 AND 100°C

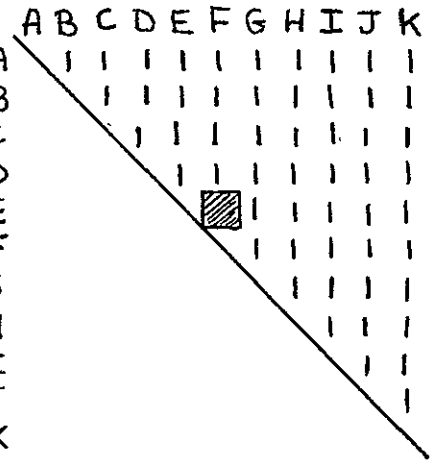
	AVERAGE RANKED ORDER	BROWNING VALUE	
	TEMP/TIME		
A.	100 / ½	3.9	A
	0	3.5	B
	110 / ¼	3.8	C
	110 / ½	4.9	D
	100 / 1	7.6	E
	100 / 1½	8.5	F
	110 / ¾	7.3	G
	100 / 2	9.0	H
	100 / 3	9.3	I
	110 / 1½	9.9	J
	110 / 1	9.7	K
	100 / 4	9.5	L
	100 / 5	10.0	M
	110 / 2	10.7	N
	110 / 2½	11.0	O
	110 / 3	11.0	P
	110 / 4	11.0	Q
	110 / 5	11.6	R
	110 / 6	12.0	S



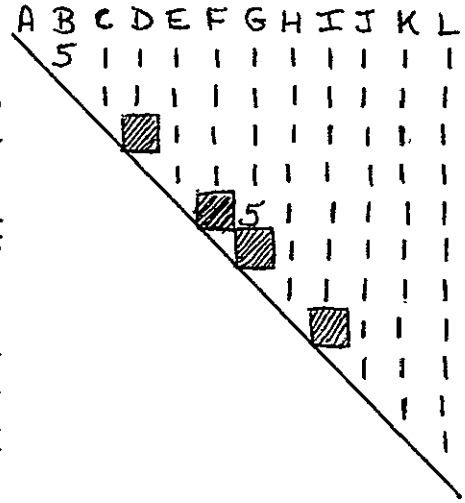
B.	90 / ½	2.4	A
	0	2.5	B
	90 / 1	3.0	C
	90 / 1½	4.6	D
	110 / ¼	3.8	E
	90 / 2	5.1	F
	110 / ½	4.9	G
	90 / 6	9.3	H
	110 / ¾	7.3	I
	110 / 1½	9.9	J
	110 / 3	11.0	K
	110 / 6	12.0	L



AVERAGE RANKED ORDER	TEMP/TIME	BROWNING VALUE
C.	90 / ½	2.4
	0	2.5
	90 / 1	3.0
	90 / 1½	4.6
	100 / ½	3.9
	90 / 2	5.1
	100 / 1	7.6
	90 / 6	9.3
	100 / 1½	8.5
	100 / 3	9.3
	100 / 5	10.0



D.	0	2.9	A
	0	3.1	B
	80 / ½	3.4	C
	80 / 2	3.8	D
	100 / ½	3.9	E
	80 / 4	5.7	F
	80 / 6	6.3	G
	80 / 7½	6.6	H
	100 / 1	7.6	I
	100 / 1½	8.5	J
	100 / 3	9.3	K
	100 / 5	10.0	L



▨ = No Significant Difference

1 = Significant Difference at 1% level

5 = Significant Difference at 5% level

TABLE 6

Visual Ranking and Browning Values for Heated Freeze Dried Apple Slices

	80°C		90°C		100°C	
Rank	Time	BV	Time	BV	Time	BV
1	0	0.3	0	0.75	½	3.0
2	1	0.5	1	0.75	1	4.6
3	½	0.3	½	1.0	2½	6.4
4	1½	0.5	3	3.5	2	6.8
5	2	0.6	2½	2.3	3	9.1
6	3	1.6	2	1.75	1½	4.5
7	2½	1.8	1½	1.5		

TABLE 7

Organoleptic Evaluation of Heating of Apple Slices

	Difference test		Preference Test		Ranking Test
	Taste	Texture	#choosing preferred/total		
eated/Unheated	NSD	NSD	7/13	NSD	NSD
eated/Reg	NSD	5%	—		1%
nheated/Reg	5%	1%	12/13	1%	1%

NSD No significant difference at the 5% level.

Percentages refer to levels of significance.

Table 8: Ranking Evaluations of Heated Cantaloupe Pieces

Ranking	Treatment		A	B	C	D	Ranking[b] Value
First	no heat	A	\		1	1	.655
Second	60°C dry[a]	B		\		1	.335
Third	70°C dry	C			\	1	-.027
Fourth	65°C FD[c]	D				\	-.964

Ranking	Treatment		A	B	C	D	Ranking[b] Value
First	no heat	A	\	5	1	1	.687
Second	70°C dry	B		\		1	.211
Third	80°C dry	C			\	1	-.100
Fourth	84°C FD	D				\	-.798

[a] dry means heated in dry state

[b] ranking value range +1.03 - 0 - -1.03

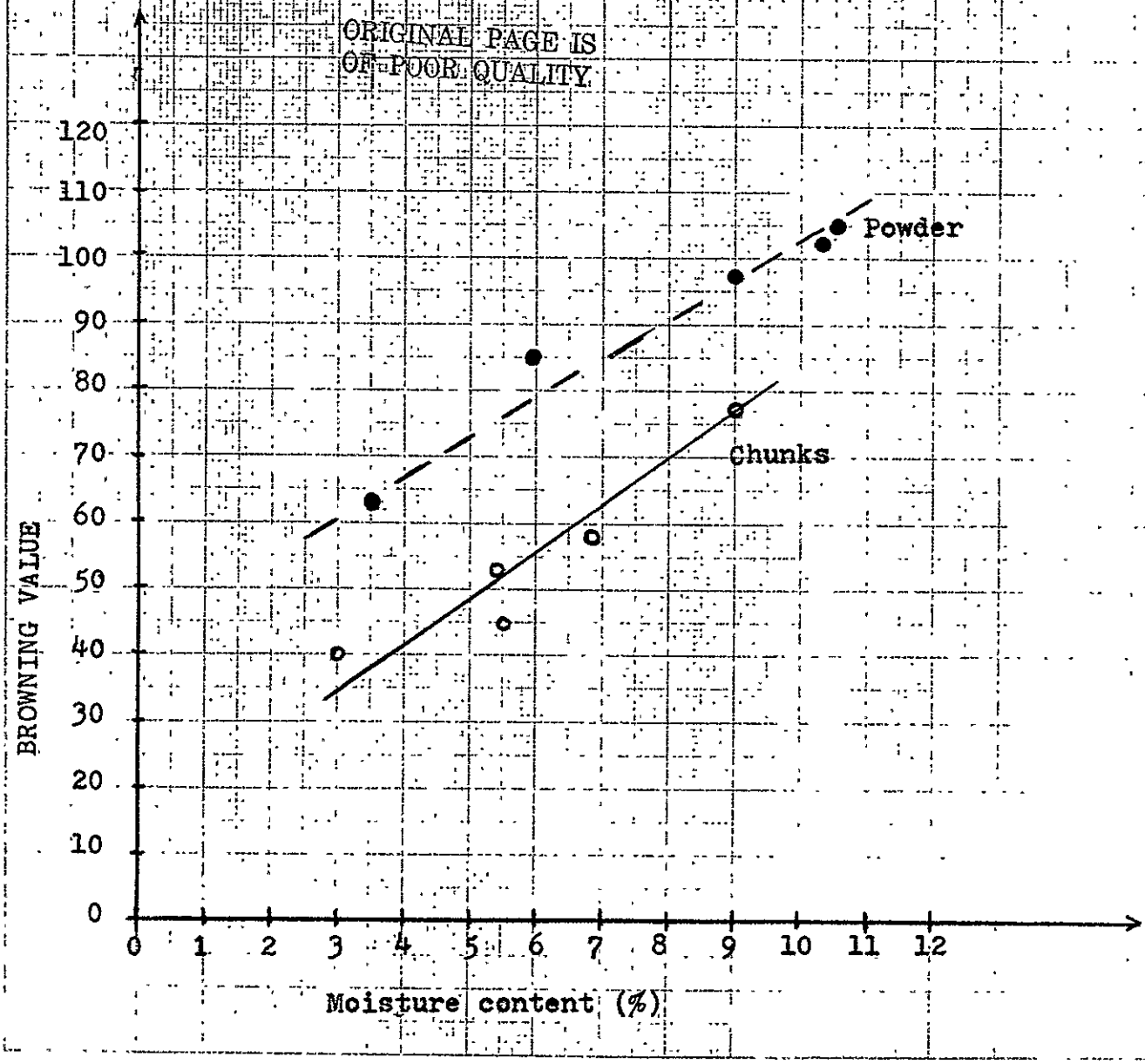
[c] peak sample temperature during freeze drying

FD means during freeze drying

Figure 1.

Browning of nonfat dry milk humidified to 32% R.H.

Comparison of browning of powder and of chunks.



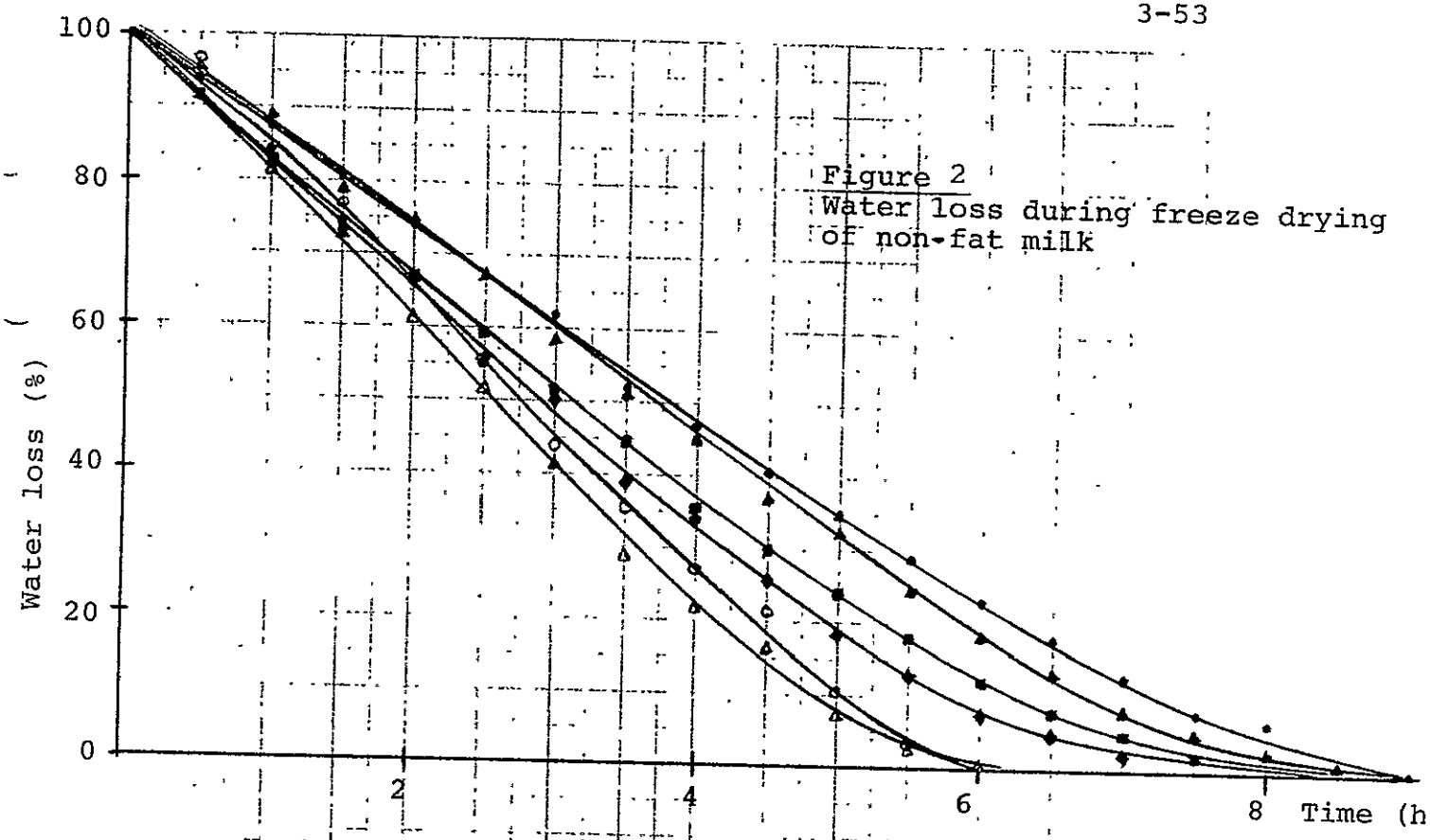


Figure 2
Water loss during freeze drying of non-fat milk

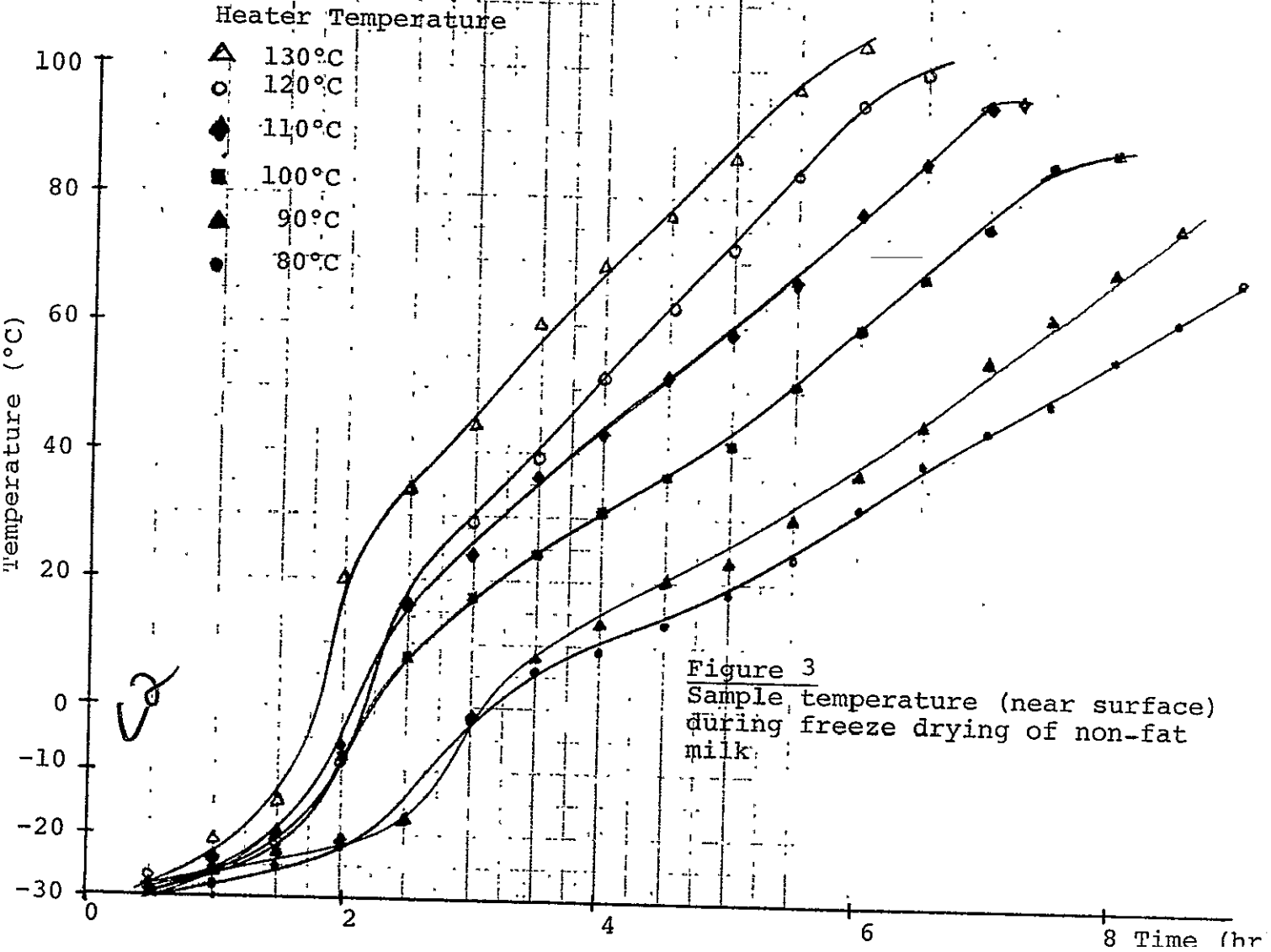


Figure 3
Sample temperature (near surface) during freeze drying of non-fat milk

Figure 4: Heating of Freeze Dried Whole Egg at High Temperature. Browning measured as optical density of Chloroform extract at 390 nm.

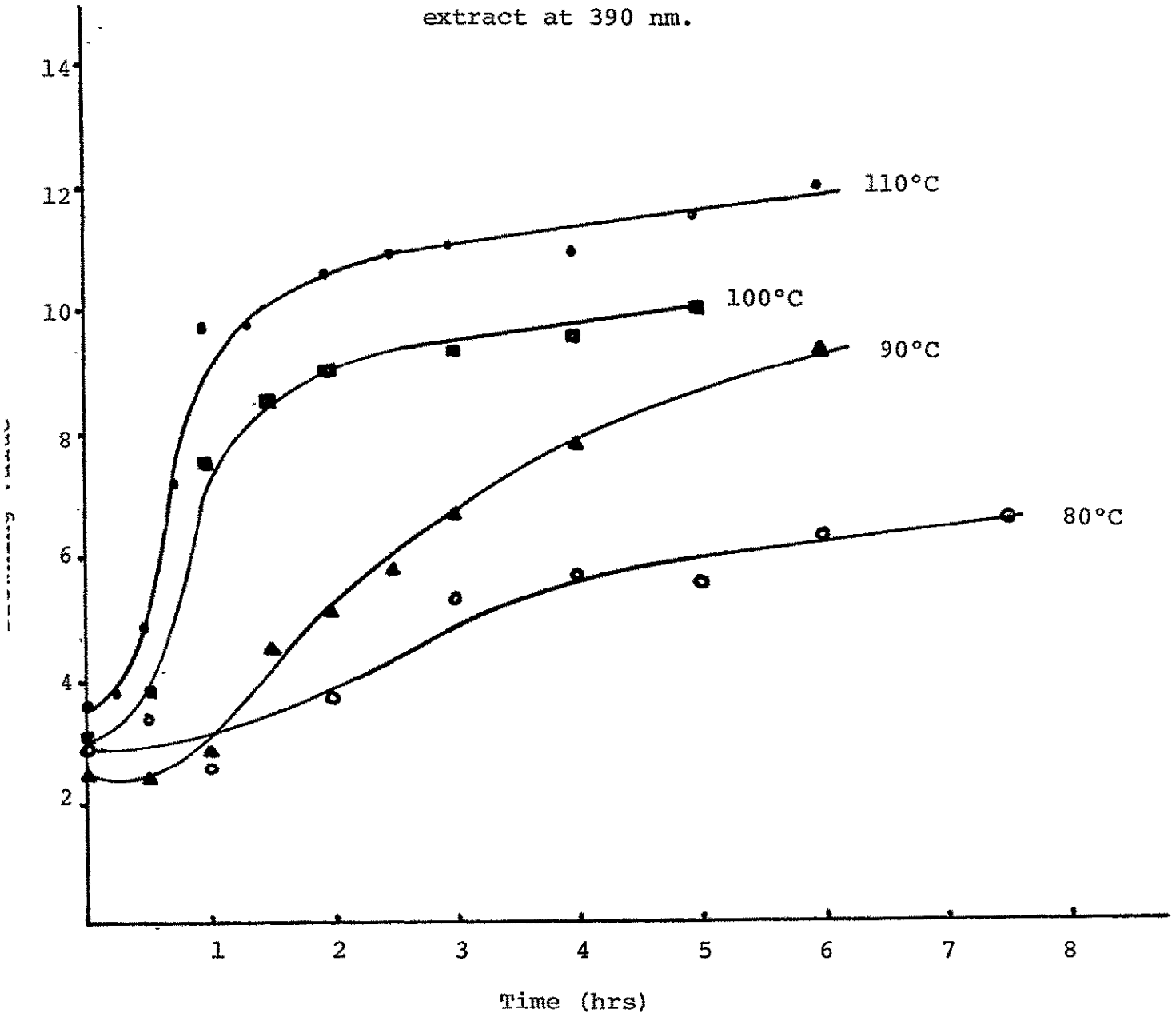


Figure 5: Heating of Freeze Dried Whole Egg at High Temperatures. Browning measured on KCl extract with Spectrofluorometer.

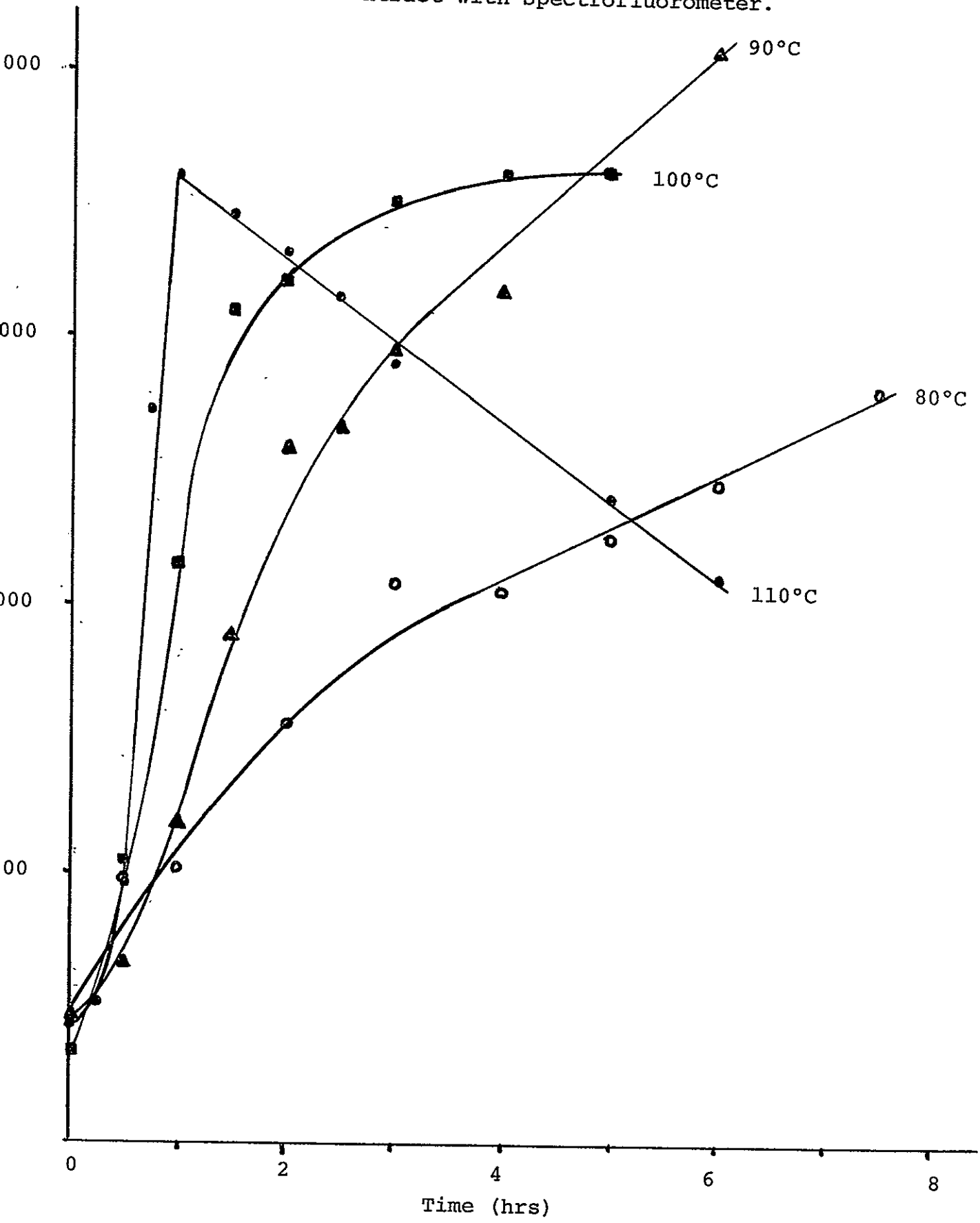


Figure 6: Heating of Freeze Dried Whole Egg at High Temperatures. Browning measured as optical density of KCl extract at 280 nm (*cloudy after dilution).

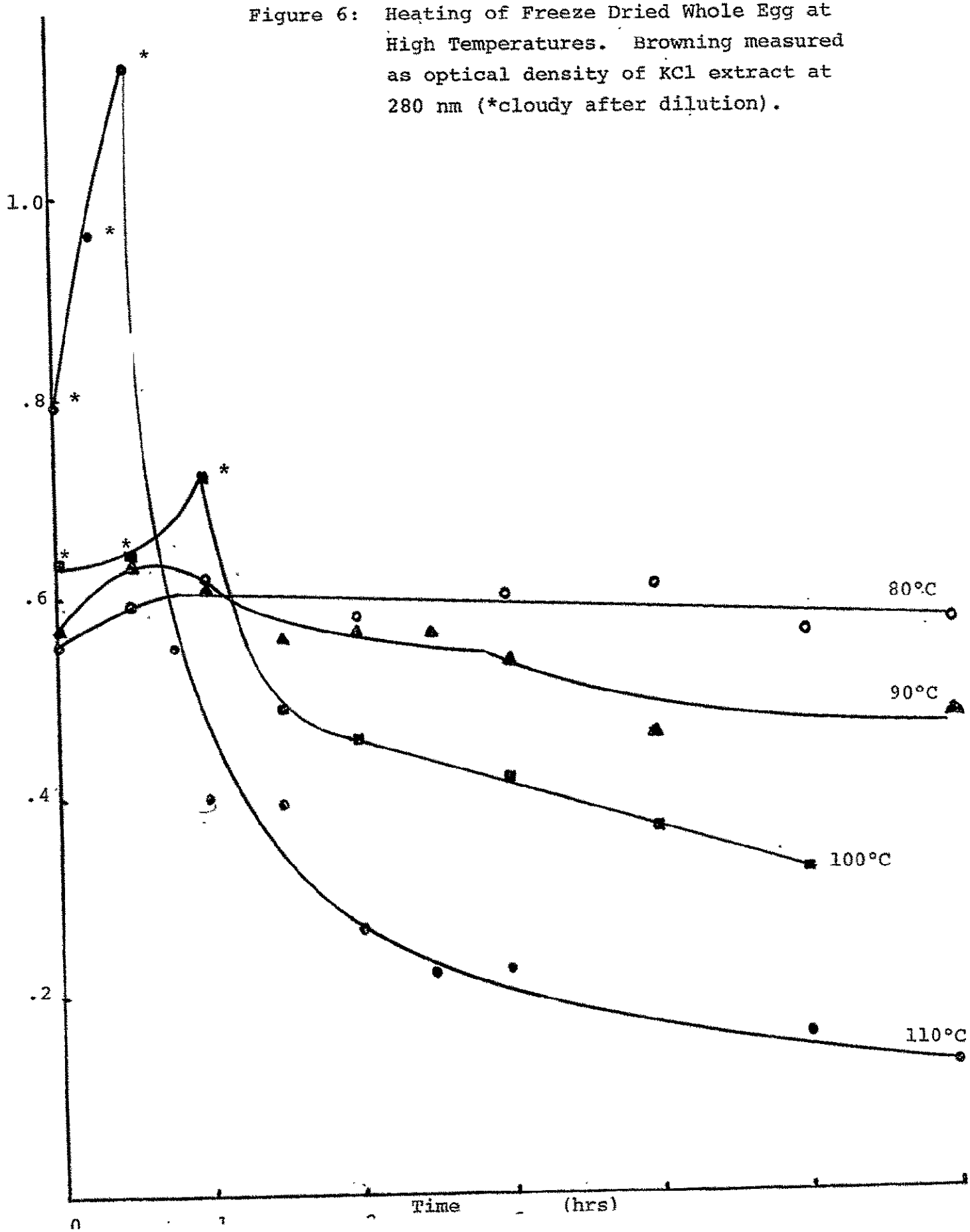
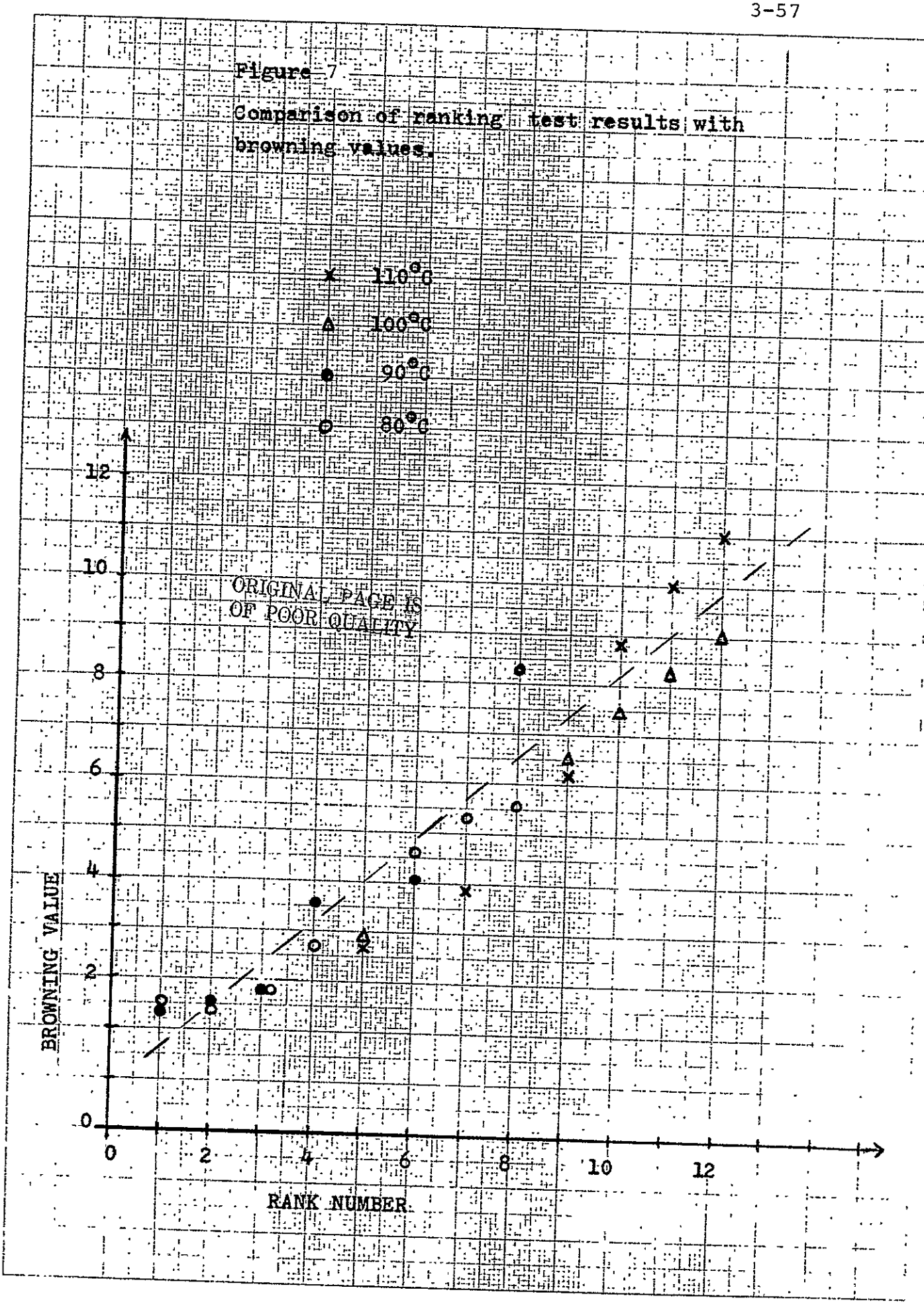


Figure 7

Comparison of ranking test results with browning values.



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4. Artificial Food Matricies (AFM)

4.1 Introduction

Work has been continued on gel systems simulating fruits and capable of preservation by freeze dehydration. Modifications and improvements have been made on the calcium alginate gel system, to give a final gel with better quality, shorter preparation time and higher processing stability. Some potential applications of the artificial food matrix in real food systems have also been evaluated.

4.2 Improvement of Sensory Quality of the AFM

We have reported previously that a vegatable- or fruit-simulating matrix was developed using calcium alginate. The matrix structure was not stable to processing either by freezing or by freeze-drying. Another defect of the calcium alginate system was its tendency towards breakdown toward the end of the mastication period. The gel showed cucumber-like, crisp texture on the first bite. However, unlike the natural cucumber which becomes more and more juicy upon chewing and breaks down smoothly in the mouth, the calcium alginate gel becomes drier and drier upon chewing, and somewhat unpleasant to swallow. It was thought that incorporation of compounds with high water holding capacity into the calcium alginate matrix may be one way of approaching the problem. Dextran, starch, sucrose and pectin were tried separately. It has been found that addition of pectin to alginate prior to the process of crosslinking with slowly diffused calcium ion resulted in a gel with much improved sensory quality.

Pectins play a major role in texture of plants and, in particular, fruits and vegetables. The main constituent within the group of pectin substances is a linear polymer composed primarily of D-galacturonic acid units linked by α-1,4 glycosidic bonds. In nature, 65%

of the carboxylic acids residues of the D-galacturonic acid moieties are esterified with methanol. They are soluble, colloidal materials which can absorb large quantities of water. This is probably the major reason why the addition of pectin to the calcium alginate system improved the sensory quality of the resultant gel.

4.3 Modification of Gelling Procedure

In previous studies the formation of AFM from sodium alginate and calcium lactate was achieved in a one step process, that is the cross-linking of Ca^{++} with COO^{-} groups of sodium alginate. In order to get a successful gel, Ca^{++} ion has to diffuse slowly into the alginate solution. At room temperature, a piece of calcium alginate gel approximately 1" in diameter, 2 1/2" in length took more than 60 hours to form. To shorten the time required for the one-step gelling, a two step gelling procedure has been developed. In the two step gelling procedure, the cross-linking reaction resulting from controlled diffusive contact of the sodium alginate mixture with calcium ions from the calcium lactate solution is preceded by a thermal gelling step obtained by incorporation of gelatin into the sodium alginate-pectin mixture. The method of preparation of these systems involved chilling the gelatin-containing alginate-pectin mixture without interferring with the subsequent cross-linking of the alginate and calcium ions. This soft gelatin gel is sliced and then placed at room temperature into calcium lactate solution directly to obtain the required alginate gelling. Since there is no longer a need for containers to hold the alginate mixture, the surface/volume ratio of alginate in direct contact with calcium ions is thus greatly

increased, and the required gelling time greatly reduced. The gelling time for this two-step gelling procedure depends on the size of the soft gelatin slices, which can be varied easily according to needs. Strips with dimensions approximately 1.0 cm x 2.0 cm x 6.0 cm take about 10 hours to form. A study to correlate size with rate of gelation is planned.

Textural quality of the fresh and freeze-thaw gels was satisfactory, appearing equal to the better quality samples obtained earlier with the non-thermally pre-gelled process.

To obtain satisfactory texture properties for the freeze dried rehydrated sample, it was thought necessary to change the composition to give a better processing stability. Through organoleptical evaluations a basic gel composition of

sodium alginate	2.5% (w/w)
pectin	2.0% (w/w)
gelatin	1.5% (w/w)
avicel	0.5% (w/w)

was chosen as being most satisfactory. Sucrose was added to some of the gels to alter the texture and provide sweetness.

The advantages of the two-step gelling procedure over the straight forward one step gelling are:

a. Reduced gelling time required

b. Simplified preparation - no container and nylon membranes are needed.

c. Flexibility - size and shape of the final gel can be varied easily according to needs instead of being limited by the size and shape of containers used.

These advantages of the two-step gelling procedure make it possible to scale up the production of the gels, which is very important for studies of the behavior of AMF in various food systems.

4.4 Causes and Minimization of Freezing Damage

Generally speaking, previous progress made in obtaining fresh gels with fruit characteristics was good. However, substantial problems were encountered in the attempts to freeze dry the gel structure. Freezing and thawing caused substantial deterioration of the gel texture and attempts to freeze dry the gels resulted in poorly rehydrating and unpleasant, rubbery texture. This is not unique to the artificial gels only, since many fruits and vegetables lose their textural qualities after freezing and thawing or freeze drying. Damage may occur during freezing, drying, storage and reconstitution. Such damage, which is cumulative, becomes apparent when the rehydrated product is eaten.

Finkle (1971) believes that the large ice crystals which are formed at the intermediate sub-zero temperatures are responsible for tissue damage. The general belief is that in plant tissue intracellular ice crystals develop at slower freezing rates. This type of freezing dehydrates the cells, thereby enlarging the intracellular spaces. Ice crystal enlargement to many times the size of individual cells, disrupts cell membranes and middle lamella, etc., causing textural changes. Levitt (1966) hypothesized that freezing damage is due to proximity of macromolecules caused by water loss during freezing. In the case of proteins, this proximity favors the formation of

disulfide bonds which cause product distortion upon rehydration. In polysaccharides other types of bonds may form. Freezing and desiccation damage are analogous in that both are attributed to water loss from vital positions in the cell.

An approach to minimizing damage is through use of protective agents. An ideal protective agent would preserve biochemical integrity of internal structures, prevent shrinkage below a minimum size, and be non-toxic and edible, as well as minimize any change in the organoleptic properties. It has been suggested that forming hydrophilic polymers within the tissue before dehydration can mechanically improve the appearance and textural qualities of some dried products (Schwimmer, 1969). Shipman et al (1972) found improvement of the texture of dehydrated celery (either air dried or freeze dried by glycerol treatment). It has been generally believed that protection against freezing injury requires permeation by the additive, but Mazur et al (1974) have found that this supposition is not valid for the survival of frozen and thawed bovine red cell.

Mohr (1974) studied the freeze-thaw (and blanch) damage to vegetable ultrastructure. He found that subcellular structures were altered more drastically by blanching than by freeze-thawing. There was much less

fine structural disruption in the high starch tissue (green pea cotyledon) than in the tissues of lower starch content (spinach leaf and green bean pod) following all processing treatments. As judged by sensory evaluations, peas also underwent less textural change on processing than other tissues studied. He hypothesized that the minimal ultrastructural change observed in peas may be associated with certain cell characteristics: high starch content, abundant protoplasmic structure, and resultant low degree of vacuolation.

It seems reasonable to assume that in our gel system, the mechanical forces exerted by the expanding ice crystals during freezing are probably the most important cause of textural deterioration of the gel after freezing treatment. It is essential that we produce a gel stable to freezing and thawing before we can obtain a good freeze-dried product. In order to minimize the mechanical forces exerted by the expanding ice crystals during freezing, the following steps were tried:

a. Incorporation of Avicel into the gel system.

Avicel is a water insoluble, microcrystalline cellulose, which can create more nucleation sites, increase the number of ice crystals, and minimize the size of each ice crystal formed during freezing.

b. Partial dehydration of the finished gels prior to freezing.

Since it is thought that the mechanical forces exerted by the expanding ice crystals are probably the main cause of the textural change of the gels after the freezing process, it is natural to try partial dehydration to remove some of the free water to see whether there will be a significant improvement of texture of the frozen-thawed gels. Air drying and osmosis against a 50% sucrose solution have been tried to reduce water content about 20-30% prior to freezing. The textural improvement of the thawed gels was apparent and significant. The freeze-thawed gels are no longer cracked into pieces or mushy; instead, the texture of these pretreated, freeze-thawed gels are almost as good as fresh gels without any freezing treatment at all.

4.5 Cause and Minimized Damage due to Freeze-Drying

Organoleptic evaluation of textural characteristics conducted on fresh gels, pretreated freeze-thawed, pretreated freeze dried and freeze dried and rehydrated gels demonstrated that changes in texture noted in rehydrated freeze-dried samples are not due primarily to the freezing process, since frozen and thawed but not dried gels were acceptable. The changes therefore are presumed to be mainly related to the freeze drying or rehydration step, though perhaps in combination with the freezing step. One factor noted was that a poor quality product was invariably obtained if the gel has collapsed during freeze drying. This not only affected the appearance of the freeze-dried gels, but also extends the rehydration time significantly.

In the gel system finally selected for further evaluation, a number of possible causes for this collapse could be identified:

a) Sucrose incorporated initially in the matrix

b) Collapse of one or more of the gelling components (alginate, pectin, gelatin)

c) Surface sucrose picked up by the gel during osmosis

d) Partial melting of the frozen gel during freeze drying.

In a series of experiments in which these factors were systematically varied, it was noted that all these factors (except the macromolecular species) had some

influence.

The most disruptive factor was an effect due to an apparent melting of the gel during the early stages of freeze drying. This could be significantly reduced or prevented (depending upon gel-formulation) by chilling the frozen samples (even slowly frozen samples) in liquid nitrogen prior to insertion in the freeze dryer. Additionally, it has proven valuable to precool the freeze dryer plates for the initial drying period. The minimum length of time for which this is necessary has not been determined yet. Besides the above "melting" effect, in most cases, the rate of freezing played an important role, with rapid freezing giving somewhat increased collapse of the structure when compared to an identically treated sample which had been slowly frozen.

It was observed that when 30% sucrose was incroporated in the initial gel system, osmosis causes slightly more severe collapse than non-osmosis. It was unclear, however, if this is due to sugar pick up or water removal of the osmosis procedure. A 50% maltodextrin solution as well as a 50% sucrose solution was used for osmosis to distinguish the effect of water removal and sucrose pick up during osmosis. The time dependent water removal during osmosis was studied also.

Weight change, solids gain and water removal due to osmosis were measured (Table 1). Examination of these samples showed that, the longer the period of osmosis,

the more obvious was the collapse. With sucrose, 1.5 hours of osmosis produced a product with an apparent collapsed surface, while with maltodextrin initial collapse of the surface was observed only after 2 hours of osmosis. When identically treated samples (through the osmosis step) were frozen at different rates, the freezing rate was noted to be a very important factor affecting collapse during freeze drying, with fast frozen samples (5 and 10) having a much more serious collapse problem than the similarly treated slow frozen ones (4 and 9).

A close inspection of the samples show that one side generally tended to collapse more. In earlier studies it had not been observed whether this more collapsed side was the side in direct contact with calcium lactate solution during cross-linking or was the newly exposed surface obtained due to slicing the cross-linked gel to reduce piece size. Contact with the sample holder during freeze drying required consideration also.

From Table 2 the freezing rate is again shown to be the most important factor affecting collapse of the freeze-dried gels. It appears immaterial with respect to collapse whether during osmosis the surface was orginally surrounded by calcium solution during cross-linking or is newly exposed after cross-linking. Additionally, no effect of sample holder was noted.

4.6 Sucrose in the Gel System

From a mass balance on the gels at various stages in the process, a number of observations have been noted. During the time in which the gel components are initially dissolved, significant water evaporates so that the initial gel concentration increases over that initially designated. Studies on the behavior of the system during the thermal gelling and cross-linking steps were conducted. A comparison of solute loss from thermally-set gels shows that during the chemical gelation step in which the thermally-set gel is crosslinked, about 70% of the sucrose is able to diffuse from the matrix. In contrast only 50% of the sucrose is lost when the thermally-set gel is exposed to pure water for an equivalent length of time.

It was further noted that sucrose was able to diffuse out of the cross-linked matrix. It appears that there may be competition between sucrose and calcium ions for binding sites of the alginate molecules, or that structural changes associated with the formation of the cross-links permits increased sucrose diffusion. It was further noted in the most recent tests that some loss of weight occurs in sucrose-free samples when soaked in water, presumably due to loss of ash associated with the gelatin or perhaps even to loss of gelatin. If it is loss of gelatin it is presumed that this is due to surface solubilization of the lower MW

gelatin fractions. Diffusion of gelatin in the matrix is not known but seems unlikely.

The optical microscope has been used to obtain some preliminary views of the structure of the freeze-dried gel matrix. It appears by polarization microscopy that a part of the gel structure following freeze drying is in the crystalline state. It is not known at present if this is the sugar component, or perhaps related to organization of the gelled system.

4.7 Applications of the AFM in Real Food Systems

Organoleptic evaluations have been initiated on products containing the artificial food matrices. In the current tests the artificial food matrices have been used as a substitute for fruit products. Comparisons are made with products containing freeze dried fruits prepared in our studies on development of improved fruit products, or to equivalent commercially available products. The organoleptic tests used are a difference analysis having a six point scale running from excellent (6) to very poor (1), and ranking preference in which samples are ranked in order of preference with the most preferred first. The organoleptic scores are presented in Table 3.

The results of the organoleptic tests are summarized briefly below:

Test 1: No significant difference between the samples at 5% level of significance.

Test 2: No significant difference at 5% level. The appearance of the AFM in the jello is more regular and "neater" than either of the real fruits. Texture of AFM noted to be different from fruits, but not unpleasant.

Test 3: No significant difference at 5% level for taste or texture. Ranking test has sample

with freeze dried fruit superior to other two.

Test 4: No significant differences. Freeze dried yogurt can make a nutritious good tasting snack. AFM pieces remain crisp while real fruits become chewy.

Test 5: Yogurt with real fresh bananas is superior. No difference between the freeze dried systems. Banana texture is more difficult to duplicate with AFM. AFM does not discolor due to enzymatic browning in contrast to bananas.

Test 6: Rehydration of AFM with pineapple juice gives improved product. Yogurt with canned pineapple clearly superior (juicier). AFM yogurt superior to commercial product.

These results are quite encouraging. Only fresh banana and canned pineapple were statistically rated better than the artificial food matrices which had been freeze dried and rehydrated. Further it should be noted that a number of advantages were noted when using the AFM:

a) Controllable size and shape which were more uniform than freeze dried fruits.

b) No discoloration problem.

c) When in dry products, less chewy or sticky (to teeth), more crunchy.

Some organoleptic tests using difference analysis having a nine point scale running from like extremely (9) to dislike extremely (1), and ranking preference are performed. The organoleptic scores and results are summarized as follows:

	Organoleptic Score			
	Taste	Texture	Appearance	Ranking
Test 1: Cherry Cake				
Cake w/ cherry pieces	7.25	7.06	7.69	0.48
Cake w/ AFM (FD+R)	5.88	6.56	7.25	-0.21
Commercial cherry cake	6.31	6.31	7.31	-0.27
Test 2: Lemon Cake				
Cake w/ AFM (FD+R) (color added)	7.29	6.77	7.62	0.30
Cake w/ Lemon rind	5.50	5.77	7.23	-0.61
Cake w/ AFM(FD+R) (no color added)	7.29	7.38	7.31	0.30

Test 1: Cake with real cherry is superior. No significance of the AFM system and the commercial cherry cake. The artificial cherry flavor used in gel rehydration was quite strong. People who like mild flavors prefer the mild commercial cherry cake. People who like strong flavors prefer cake with the rehydrated AFM. The overall quality and acceptability of the cakes are good.

Test 2: The taste and texture of cakes with rehydrated AFM (either with or without artificial yellow color added)

is significantly better (at 1% level) than with cakes containing lemon rind. The difference of the cakes with AFM and lemon rind in ranking scores is significant also. The cakes with AFM is superior at 1% level. The lemon rind has a bitter taste, which makes it less desirable than cakes baked with AFM.

It has been noted that after baking, the texture of the gels are more soft and uniform. One possible explanation is that some of the gelatin was melted during the baking process and redistributed in a way that gave a better final texture.

4.8 Preliminary Storage Test

Freeze dried yogurt with orange pieces or AFM (with artificial orange flavoring) and freeze dried commercial orange yogurt were evaluated organoleptically immediately following production. Samples were then stored for two months in glass jars (in darkness) at room temperature. Organoleptic evaluations were conducted at the end of the two months.

No deterioration was observable after two months storage at room temperature. The results of the organoleptic evaluation before and after storage are shown in Table 4.

Before storage there was no significant difference in taste. However, freeze dried yogurt with real orange was judged superior to the commercial yogurt with regard to texture and overall ranking (5% level of significance).

This preliminary storage test is indicative that freeze dried food items containing AFM can be stored without undesirable deteriorative changes.

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Table 1

Changes in Gel Composition Due to Osmosis against Sucrose or Maltodextrin

Code No.[a]	Medium used for osmosis	Time (hr) of osmosis	Wt. change (%)	Sugar gain g/100g gels	Water removal g/100g gels	Sugar content after osmosis
1	50% sucrose	0.5	14.2	2.7	16.9	20.7
2	"	1.0	17.2	4.1	21.3	23.1
3	"	1.5	24.4	4.3	28.7	25.5
4	"	2.0	24.9	4.6	29.5	26.0
6	50% maltodextrin	0.5	18.1	-2.2	15.9	15.6
7	"	1.0	23.1	-2.0	21.1	17.0
8	"	1.5	26.4	-1.9	24.5	17.9
9	"	2.0	26.8	-2.0	24.8	17.8

Initial system: 30% sucrose, 2.5% alginate, 2.0% pectin, 2.0% gelatin, 0.25% avicel

a) Samples 5 and 10 were treated identically to samples 4 and 9 respectively, but were fast frozen prior to freeze drying. Samples 1-4 and 6-9 were slowly frozen.

Table 2

Effect of Sugar Content and Freezing Rate on Collapse of the Gels

Code No.	# of new surfaces[a]	Osmosis	Sugar content %[b]	Solids gained g/100g gel	Water removed g/100g gel	Freezing rate	Collapse index[c]
1	0	+	20.1	3.8	20.2	slow	0
2	0	+	20.1	3.8	20.2	fast	1.0
3	1	+	21.3	5.0	20.6	slow	0
4	1	+	21.3	5.0	20.6	fast	1.0
5	1	-	12.9	-	-	slow	0
6	1	-	12.9	-	-	fast	0.5
7	2	+	22.1	5.1	22.7	slow	0.5
8	2	+	22.1	5.1	22.7	fast	1.0
9	2	-	13.1	-	-	slow	0
10	2	-	13.1	-	-	fast	0.5

a) Number of sufaces during osmosis which were not in direct contact with calcium lactate during cross-linking.

b) After osmosis

c) Arbitrary scale: 0 = no collapse; 1 = slightly collapsed to 5 = seriously collapsed

Table 3

Organoleptic Scores for Product Containing Artificial Food Matrices

	Organoleptic Score		
	Taste	Texture	Ranking
Test 1 Peach Yogurt			
Yogurt w/AFM (FD+R)	4.36	3.70	-0.08
Yogurt w/FD fruit (FD+R)	3.82	4.10	-0.31
Commercial yogurt	4.64	4.20	0.39
Test 2 Strawberry Jello			
Jello w/FD fruit (FD)	4.50	3.83	0.28
Jello w/AFM (FD+R)	4.17	3.83	-0.14
Jello w/frozen fruit	4.00	4.17	-0.14
Test 3 Pineapple Yogurt			
Commercial yogurt	3.92	4.30	-0.14
Yogurt w/AFM (FD+R)	3.42	4.25	-0.28
Yogurt w/FD fruit (FD+R)	4.42	4.67	0.43
Test 4 Pineapple Yogurt (Dry)			
Commercial yogurt	3.50	3.83	-0.14
Yogurt w/AFM (FD+R)	4.08	4.00	0.23
Yogurt w/FD fruit (FD+R)	3.58	3.83	-0.07
Test 5 Banana Yogurt			
Yogurt w/fresh fruit	5.00	4.62	+0.65
Yogurt w/AFM (FD+R)	3.46	3.31	-0.33
Yogurt w/FD fruit (FD+R)	3.62	3.69	-0.33
Test 6 Pineapple Yogurt			
Yogurt w/canned fruit	5.08	5.00	0.71
Commercial yogurt	2.83	3.58	-0.50
Yogurt w/AFM (FD+R)	3.92	3.33	-0.21

Commercial yogurt = commercial flavored yogurt
Yogurt = plain (unflavored) yogurt with sugar added
AFM = artificial food matrices: rehydrated with flavor & color
FD+R = freeze dried and rehydrated

Table 4

Storage Tests of Yogurt Containing Various Orange Yogurt Products

	Taste	Texture	Ranking
Before Storage			
Freeze dried yogurt w/ real orange	6.28	5.66	0.24
Freeze dried yogurt w/ AFM	5.89	5.33	0.05
Freeze dried commercial orange yogurt	5.44	4.77	-0.28
After Storage			
Freeze dried yogurt w/ real orange	6.73	6.80	0.23
Freeze dried yogurt w/ AFM	6.47	6.40	-0.11
Freeze dried commercial orange yogurt	6.33	6.40	-0.11

5. Freeze Dried Food Products of Improved Quality

5.1 Introduction

Utilization of improvements in freeze dehydration processing suggested by research conducted in this contract has been directed to the development of dehydrated fruit products. Process variables having greatest influence on product quality are freezing rate and initial solids content.

Phase I studies evaluated methods and processes for preparing a freeze dried fruit product of improved organoleptic quality. The influence of a number of variables, but most notably freezing rate and initial solids content, on the quality of apple slices was evaluated.

Phase II studies investigated the applicability of the processes developed in Phase I to a number of additional fruit products.

Phase III studies have utilized many of the same fruit varieties as used in Phase II, and evaluated the influence of conducting the osmosis pretreatment with high and low molecular weight osmotic agents and the effect of two methods for physically contacting the osmotic fluid with the fruit samples. In Phase III studies, some of the process variables which have been shown earlier (Phase I and II) to result in inferior products were eliminated.

For completeness, this section of the Phase III annual report will include results of the organoleptic tests which have been conducted in both Phase II (Tests 1-11) and in Phase III (Tests 12-30). Also being presented are the results of the 16 week storage study of freeze dried peaches.

Also included in this section is the manuscript of a paper entitled "Process Conditions for Improved Flavor Quality of Freeze Dried Foods" which was presented at the 1974 American Chemical Society meeting in Atlantic City, New Jersey. This paper, which has been submitted for publication, contains a literature survey as well as including some of the results of the fruit studies reported upon here.

5.2 Methods

5.2.1 Sample Preparation

Fruit samples were prepared according to the following scheme:

1) The fresh fruits were washed and trimmed (peeled, pitted, etc.). (The few canned fruit samples were drained).

2) The trimmed fruit was cut into uniform pieces (generally slices) and subjected to the following treatments.

3) Osmosis

a) Fruits which were not to be osmotically treated were given a short dip in a bath of 0.52% ascorbic acid and 0.14% malic acid (to prevent browning) and allowed to drain prior to freezing.

b) Fruits which were to be osmotically treated were soaked in an aqueous solution of 60% osmotic agent (either sucrose or maltodextrin), 0.52% ascorbic acid and 0.14% malic acid. (The maltodextrin used was Maltrin-15 a 15 D.E. material from Grain Processing Co., Muscatine, Iowa). The fruit slices were contacted with the osmosis solution in two ways (circulation or vacuum infusion) to be described below. Following the osmostic treatment, the fruit is rinsed for 30 seconds to remove osmosis solution adhering to the fruit surface. This prevents stickiness after dehydration.

4) Freezing

a) For slow freezing the fruit is spread on aluminum foil which is placed on the freeze dryer sample trays, covered with additional aluminum foil and these trays are then placed in a -20°C room for at least 24 hours.

b) For rapid freezing, the rinsed fruit is immersed in a bath of liquid nitrogen and the frozen pieces then placed on the freeze dryer sample trays.

5) Freeze drying is conducted at a low chamber pressure and ambient temperature heating plates.

6) Following freeze drying, organoleptic evaluations were always conducted on the dry product and in a number of cases on a rehydrated paste produced by grinding the dry product and mixing in the desired amount of water.

5.2.2 Methods of Osmotic Treatment

It was noted above that two systems were evaluated for use in contacting the fruit slices with the osmosis solution. These have been labeled the circulation method and the vacuum infusion method.

1) Circulation method

This system consists of a conical, bottom draining polyethylene tank (either 1 or 4 liter capacity) and a centrifugal pump. The osmotic solution was drawn from

the bottom of the tank and recirculated to the top, above the level of the fruit. The fruit pieces were held continuously submerged in the solution by a porous polyethylene plate. The relative amount of fruit and solution were such that the solution concentration would not change appreciably during the process.

2) Vacuum infusion method

This system was composed of a 2 liter erlenmeyer flask with side tubulature connected to a vacuum pump. Fruit slices were placed through the flask neck which was then sealed with a fitting which connected, through a shut-off valve, to a tank containing the osmotic solution. The flask was evacuated through the side arm and when the desired vacuum was achieved, the tank shut-off valve was opened and the solution allowed to contact the fruit. In some cases the vacuum pump continued to operate following the contacting, while in others it was turned off just prior to opening the valve. No difference in behavior was noted.

3) Kinetics of water loss and solute uptake

Evaluation of the kinetics of water loss and sucrose uptake by apple slices indicate both some important differences and similarities of the two procedures. In particular, the rate of water loss does not appear to depend on presence or absence of vacuum during initial contact of the sucrose solution with the apples. In

contrast, with the circulation system very little sugar is taken up by the slice (i.e. little is retained following a 20 sec water rinse), while with the vacuum impregnation system sugar uptake results have been more variable. A typical set of curves for water loss and sugar weight gain are given in Figure 1.

Kinetic studies with the circulation system shown in Figure 1 indicate a rapid loss of water for a period of 2 hours, followed by a rapid, but decreasing rate of loss for the period 2-6 hours. Results showed that, with this system, rinsed apple slices of about 30% solids could be prepared in 4-6 hours of treatment. At this time, about 25% of the solids was added sugar.

It has also been noted that for the piece sizes utilized in these studies (between 5 and 10 mm in minimum thickness) the initial rates of water loss were relatively insensitive to rates of circulation in the apparatus, though at the intermediate times (1-5 hours) the circulation system does give some improved water loss.

One study related to the effect of steam blanching of apple slices on the kinetics of water loss and sugar uptake during the osmotic pretreatment of apple slices (Figure 2). It was noted that the blanched samples lost water more rapidly in the initial phases of the pretreatment, though the ultimate water loss was not sizably different from the unblanched slices. The amount of sugar

taken up by the slices was about twice as great for the blanched as the unblanched (corrected for differences in water loss). The uptake was very rapid in both cases, reaching the ultimate level with 1/2 hour of treatment, at which point it remained constant. Organoleptic tests which were conducted on these products showed no significant difference between blanched or unblanched apples (Table 1).

5.2.3 Organoleptic Tests

Three methods of organoleptic testing were utilized in evaluating the relative quality of the different processing conditions for a number of fruit products. The tests are completely described in Larmond (Methods for Sensory Evaluation of Foods, Publication 1284, Canadian Department of Agriculture) and will be summarized here.

Products were scored in a difference test for taste and texture using the following scale (together with numerical euqivalents): very poor (1), poor (2), fair (3), good (4), very good (5) and excellent (6). By analysis of variance, the difference between samples can be evaluated for significance. In addition, the average value of the scores can be used as a measure of the absolute product acceptability, though some particular psychological and numerical factors must be considered. As a numerical factor, the values given to the various

scores could be taken as mid-range values, to account for the fact that there are no scores granted above and below the end points. Even so, while "good" would then range from 3.5 to 4.5, "excellent" will still only have half the range, from 5.5 to 6.0. As psychological factors, there is a reluctance to grant a score of "very poor" or "excellent", as these represent to many judges an ideal. Thus, the scale in reality becomes somewhat compressed with quite good quality product having numerical values of 3-4.

In the discussion which follows on the various fruit samples, the descriptive terms associated with average product scores will be classified according to the following listing:

Score in test	Description	Range for description
6	Excellent	5.3 - 6
5	Very good	4.3 - 5.3
4	Good	3.3 - 4.3
3	Fair	2.3 - 3.3
2	Poor	1.3 - 2.3
1	Very poor	Below 1.3

A second test was a paired comparison preference test in which samples were presented in groups of two. In this case, the judge merely has to express a preference for one sample or the other. There was a provision for

expressing the degree of preference, but analysis of this information tended to follow the determined significance of the preference test. By consideration of the various combinations of paired comparisons, an overall preference can be determined.

In the third organoleptic test, all samples were presented for ranking according to overall quality. An analysis of variance on the conversion of ranks to scores results in an evaluation of ranking significance. For most tests, four samples were presented and the numerical conversion of ranks were first (+1.03), second (+0.30), third (-0.30) and fourth (-1.03). The degree to which the sample approaches +1.03 is a measure of its overall acceptance and the difference between values is a measure of the degree of preference.

5.3 Organoleptic Evaluation of Effects of Process Variables

5.3.1 Introduction

A number of process treatments have been utilized and description of individual samples has been by a code which is presented below. The order of the final code is: solids content/contacting/freezing rate.

Code letter	Process condition
I	Increased solids, sucrose
MI	Increased solids, maltodextrin
N	Normal solids
V	Vacuum infusion contact
no letter	Circulation contact
S	Slow freezing
F	Fast freezing

Thus IS is sucrose osmosis by circulation with slow freezing, while MIVS is maltodextrin osmosis by vacuum infusion and slow freezing.

The results of the organoleptic evaluations are presented in a series of tables (2-4). The scores of the difference tests are presented in Table 2, the numerical evaluations of the ranking tests in Table 3 and the summarized statistical significances of these two tests, plus the results of the preference tests in Table 4.

In the following discussions the trends which are noted in these tabulated results are presented. Some of these trends are statistically significant at various

levels and some show "no significant difference" when analyzed by statistical methods. The statistical significance of the trends which are discussed can be noted by referring to the table which summarizes the statistical evaluations for the various organoleptic tests (Table 4). It is felt that a qualitative discussion of trends is useful and necessary as a supplement to the statistical data.

5.3.2 Evaulation of Fruit in the Dry State

(Numbers in parenthese refer to sample numbers in Tables 2-4).

1) Cherries (1)

Fresh cherries were pitted and halved prior to use in the test procedures. The cherry samples thus had a heterogenous geometry, in that about 1/2 of the surface area was covered with the skin. This might be expected to influence sample shape if structural collapse should occur. It can be further noted that cherries have a high natural carbohydrate content (about 15%).

All the samples had shrivelled following freeze drying, most likely due to collapse and uneven shrinkage. This resulted in a product of poor appearance and of somewhat leathery texture, which was not well received. With respect to taste, all samples were judged to be only "fair" and there was no significant differences between any of

the processes.

These results reflect the generally poor quality of the freeze dried cherries, which apparently is due to (1) the presence of the skin (low water permeability) impeding some vapor flow and (2) the combined effect of a high level of low molecular weight carbohydrates and a low level of higher molecular weight structural carbohydrates in the raw fruit. Typical values from the Heinz handbook of Nutritional Data shows the following trends for some fruits:

Fruit	Total Carbohydrate	Crude Fiber	Ratio of Total Carbohydrate to Crude Fiber
Cherries	14.8	0.3	49
Bananas	23.0	0.6	38
Peaches	12.0	0.6	20
Apples	14.9	1.0	15
Cantaloupe	4.6	0.6	7.7

While not necessarily equal to non-structural and structural carbohydrates it is noted that fruits which are difficult to freeze dry have high ratios of total carbohydrate to crude fiber. Thus procedures which result in higher levels of non-structural carbohydrate will not result in an improved product, as was observed in the tests.

2) Honeydew melon (2)

Tests with honeydew melon showed that slowly frozen samples were preferred to rapidly frozen samples. There was essentially no difference noted with respect to initial solids content for the slowly frozen samples. For taste the slowly frozen samples were rated as "good" while the two rapidly frozen samples were rated as "fair". Little difference was noted in texture (rated as "good") with the exception of the fast frozen osmotic pretreated sample which was rated as "fair".

3) Cantaloupe (3,5,18,19)

Osmotically pretreated, slowly frozen freeze dried cantaloupe was a well received product generally being rated "very good" for taste and "good" for texture. There was no clear indication if osmotic treatments utilizing sucrose were more or less effective than using maltodextrin. Untreated cantaloupe, which always was ranked lowest in taste, was nevertheless, generally classified as "good" in taste. Rapid freezing of sucrose treated samples appeared to result in degraded texture compared to the other samples, resulting in low ranking and preference scores.

4) Strawberries (4,6,20)

Sucrose treated slowly frozen strawberries were evaluated as having taste and texture on the border between

"good" and "very good". All other types of strawberry samples rated between "fair" and "good". In all studies, the sucrose treated, slowly frozen samples were ranked and preferred as the best. Little difference was noted between the samples processed by the other procedures.

5) Pears (8,11)

The results obtained for the various treatments using pears were somewhat variable. The poorest sample was the sucrose treated, fast frozen processed. All other samples were rated as "good" and in one case the sucrose treated, slowly frozen samples were classified as "very good".

6) Pineapple (10,29,30)

Fresh pineapple chunks were used in one test (#10), while the remaining tests (#29,30) were conducted with a commercial thermally processed pineapple product (packed in pineapple juice). For the fresh product, the sucrose treated, slowly frozen material was rated highest, being "very good" in taste and "good" in texture. Other samples were rated as "good" or "fair". In the ranking and preference evaluations, the sucrose treated, slowly frozen samples were clearly superior.

For the sample prepared from canned pineapple chunks, the results are different. The preferred process in this case is slow freezing alone (i.e. no osmotic pretreatment) which was rated as "very good" in taste and texture.

The sucrose treated sample is still quite acceptable (rated as "good"). Use of maltodextrin as the osmotic agent resulted in samples of "fair" to "good" ratings.

The variability of preference is apparently due to the differences of the initial fruit (raw vs. canned) and its response to flavor and texture modification due to the process. Canned pineapple, which has been in contact with an excess of juice and treated (heating) so as to alter cell permeability to solutes (such as juice solubles), can be considered to have undergone a type of pretreatment which should alter its initial solute distribution when compared to raw pineapple. At the same time, overall fruit structure is essentially retained, though it may have changed somewhat. For these reasons, when canned pineapple was utilized as the feed material, additional osmotic treatments did not lead to the improvements which were observed with the fresh pineapple. Additionally, the sweetness level of canned pineapple is higher than for fresh pineapple, and it must also be considered that the reduction in ratings of the sucrose treated sample might be due to an overly sweet product.

7) Apples (12,14,15,16)

In all studies conducted with apples, the sucrose treated, slowly frozen samples were clearly superior. They were generally rated as "very good" in taste and "good"

in texture. The slowly frozen samples which were not osmotically pretreated were rated as only "fair". In all the rankings and preference evaluations, the osmotically pretreated samples prepared with sucrose were preferred over the maltodextrin osmotic treated or the untreated samples.

8) Peaches (9,17,22,24,25,27,28)

Freeze dried peach slices are generally satisfactory products, on most occasions rating a "good" or better, independent of processes. However on almost all test occasions the osmotically treated samples were rated higher, often being characterized as "very good". The only samples which rated as low as "fair" (for taste) were some which were not osmotically pretreated. With respect to texture, variable results were obtained relative to the improvement with the osmotic treatment, most likely due to differences of maturity of the raw fruit. The textures obtained are for the most part better in rating than the untreated samples. Ranking evaluations show a clear preference for the osmotically pretreated samples, though often the degree of discrimination is relatively small. Preference studies show the same results.

5.3.3 Evaluations of Fruit as Dry or Rehydrated Products

1) Cantaloupe (3,7)

Rehydration of cantaloupe samples resulted in a reduction of the taste scores, with the slowly frozen samples remaining the preferred. Taste scores ran from barely "good" for the osmotically pretreated, slow frozen sample (dry rating was "very good") to "fair" for the other three samples. Texture is not evaluated for the rehydrated samples, and this fact resulted in the strong reversal in the rankings of the two fast frozen samples. The osmotically treated sample had a poorer texture dry than the untreated sample, which resulted in its being ranked last in the dry state. In both the rehydrated and dry states the osmotically treated, slowly frozen sample was preferred and ranked as best.

2) Strawberries (20,21,23)

Taste scores for the various strawberry samples remained almost unchanged between dry and rehydrated tests. The sucrose treated, slowly frozen samples were ranked at the top of the "good" category (i.e. almost "very good") while the maltodextrin treated and untreated samples were much lower in the "good" ratings. The order of ranking the samples remained unchanged, though the differences between sucrose and maltodextrin samples

decreased. The degree of preference for the osmotically treated samples was lower, though these samples were still the preferred.

3) Peaches (25,26)

Peach slices were osmotically pretreated with sucrose according to two procedures, a vacuum infusion method and a circulation method. The circulation osmosis product gave the highest taste scores ("good") in both the dry and rehydrated states. While the untreated sample was rated essentially the same in both the dry and rehydrated states, the sample which was osmotically treated by vacuum infusion showed a decrease in taste score, placing it much lower than the non-treated. The reason for this change in acceptability of the vacuum infused sample upon rehydration is not known. Ranking and preference behavior closely paralleled the taste scores.

4) Apples (12,13)

Organoleptic evaluations of freeze dried apples in the dry and rehydrated states give essentially identical results. The sucrose treated, slowly frozen samples were rated "very good" in either presentation and according to preference evaluations, these samples were greatly preferred.

5.3.4 Organoleptic Evaluation of the Osmotic Treatment

1) Vacuum Impregnation vs. Circulation

Comparative studies between vacuum impregnation and circulation systems have been conducted using sucrose with apple slices (15) and peach slices (25) and using maltodextrin with pineapple chunks (30). With the sucrose samples, there was essentially no difference between the process when evaluated by any of the three organoleptic tests. In both cases, the osmotically treated samples rated higher taste and texture scores, ranks and preference when compared to untreated samples.

With the maltodextrin treated pineapple chunks, the opposite behavior was observed. The circulation prepared sample was clearly inferior to the vacuum prepared. It has already been noted that the canned pineapple chunks which were freeze dried without osmotic treatments were found to be more acceptable than the treated samples.

2) Maltodextrin vs. Sucrose as on Osmosis Agent

For a number of the fruits, both maltodextrin and sucrose were tested as osmotic agents. While most of the studies were conducted using the circulating system (16,17, 18,24,29), one sample was tested using both osmotic agents in the vacuum impregnation system (27). With respect to the circulating system, and omitting the canned pineapple sample (29) for reasons already noted, it is observed that in all cases taste and texture scores for sucrose

treated samples are higher than their maltodextrin counterparts. In two of the four tests the preference and ranking evaluations are decidedly in favor of the sucrose treatments. These results show that in the circulating system, the osmotic treated samples are generally preferred, with the sucrose being considered better.

With vacuum impregnation, little difference was found between the samples, though there was a slight preference and higher ranking for the osmotically treated materials. There was little difference between the sucrose and maltodextrin.

5.4 Storage Stability of Osmotically Treated Fruit Slices

5.4.1 Introduction

Studies on the storage stability of freeze dried osmotically treated slowly frozen fruit slices have been initiated in the Phase III period. Temperature and water content are the parameters investigated. One study with peach slices has been completed and a similar study with apple slices was initiated. Additionally, samples of apple slices which were retained from the lot sent to the Manned Spacecraft Center as part of end items of Phase I were evaluated after 10 months of storage.

The evaluation of stability of these freeze dried products is necessary to develop information on the maximum values of temperature and moisture which can be tolerated during storage. This information will be utilized in conjunction with mass transport kinetics of packaging materials to define expected storage life for various packaging configurations and storage conditions

5.4.2. Methods

To evaluate the storage stability of osmotically pretreated freeze dried peaches, samples were prepared by 3 hour osmosis pretreatments in either a 60% sucrose solution or a 45% maltodextrin (Maltrin-15, Grain Processing Co.) solution. Malic acid (0.14%) and ascorbic acid (0.52%) were included in the solutions. Following freeze drying

the samples were equilibrated at three water activities (0, 0.11 and 0.43) and then sealed into containers for storage at 22° and 37°C. Control samples were stored dry at 4°C. Organoleptic evaluations of the stored products are being conducted according to the schedule in Table 5. The time schedule for evaluation is identical for the maltodextrin and sucrose treated samples. Rehydrated samples are prepared as a slurry (60% by weight as water) to eliminate influences of texture.

Two methods of organoleptic testing were utilized in evaluating the relative quality of the different processing conditions for a number of fruit products. The tests are completely described in Larmond (Methods for Sensory Evaluation of Foods, Publication 1284, Canadian Department of Agriculture).

Products were scored in a difference test for taste and texture. In contrast with our evaluation scale used with the freeze dried fruits (not stored) in which 6 points covered the range of "excellent" to "very poor", the difference tests for these studies have been altered by expanding the scale describing quality such that it now goes from "dislike extremely" (1) to "like extremely" (9), with 5 being "neither like not dislike". The test form is present as Table 6.

By analysis of variance, the difference between samples can be evaluated for significance. In addition, the average value of the scores can be used as a measure of the absolute product acceptability, though some particular psychological and numerical factors must be considered. These are discussed earlier in this section.

In the second organoleptic test, all samples were presented for ranking according to overall quality. An analysis of variance on the conversion of ranks to scores results in an evaluation of ranking significance. Difference and Ranking tests are being used on both dry and rehydrated samples.

5.4.3 Results of Storage Stability Studies

Apple Slices - Some cans of apple slices which had been freeze dried in February and March of 1973 as part of the Phase I end items had been retained at M.I.T., and these were evaluated for organoleptic quality after 10 months storage. These apple slices had been osmotically treated with sucrose and slowly frozen prior to freeze drying, and stored for 10 months at room temperature in tin cans sealed while under vacuum. On a 6 point scale (1 = very poor, 6 = excellent), the taste score was 4.45 ("very good"), while the texture was 3.55 ("good"). These values are comparable to typical values obtained on similarly processed apple slices evaluated immediately following freeze drying (taste = 4.6; texture = 4.7).

Peach Slices - Tabulated data for the taste and texture scores for the dry and rehydrated products are given in Table 7 and the ranking evaluations are presented in Table 8. Typical examples of statistical significance of the data in Tables 7 and 8 are given in Tables 9 and 10. The amount of information contained in Table 7 makes comprehension difficult, so various aspects of that Table are presented in Figures 3 and 4. Figure 3 presents the scores for taste and texture for the sucrose and maltodextrin samples evaluated in the "dry" state. An arbitrary designation of a score of 4.5 as the limit of acceptability is indicated. (This is approximately the score of neither like or dislike on the test form). It is easily seen in Figure 3, that the most important factor governing storage stability of the dry product is the sample moisture content. There is also a slight apparent effect due to temperature for the low humidity samples (0 or 11% RH). In almost all cases, the samples which were vacuum packed and stored at 22°C had the highest scores, indicating that oxygen also has an effect on storage stability. The influence of the storage conditions were more pronounced on the evaluation of taste than on texture, with the exception of moisture content. Furthermore, the sucrose treated samples were somewhat more sensitive to moisture content than the maltodextrin treated.

The same influences as noted above are also seen in Figure 4, in which flavor scores are compared for sucrose and maltodextrin treated samples evaluated in the dry and rehydrated states. Again moisture content is the most

important environmental factor, especially when evaluation is conducted in the dry state. It was noted that upon rehydration the flavor scores of the high moisture samples were greatly improved. This most probably is due to dilution of the undesirable taste components. In evaluations in the rehydrated state there is also an improvement in flavor score for sucrose-treated samples, which were stored under vacuum, but this improvement was absent in maltodextrin-treated samples.

Ranking evaluations in Table 8 demonstrate the same phenomena as noted above, the high humidity samples are generally ranked the lowest, with 37°C samples generally lower than the 22°C. In almost all cases, the vacuum sealed sample was ranked first and for the low humidity samples, the influence of temperature was slight. Usually there was only a trend toward ranking the 37°C samples lower than either the 4 or 22°C.

From the results given above for the range of temperatures and moistures studied, the following observations can be made:

1) Moisture content is the most important factor determining loss of product quality. Storage at a water activity of 0.43 gives an undesirable product with respect to both taste and texture. Storage at a water activity of 0.10 gives a good product.

2) For samples at low water activity (0 or 0.10) there was little difference in acceptability

between samples stored at 4 or 22°C. These had somewhat better scores than samples stored at 37°C, though storage at all three temperatures gave acceptable products.

3) Storage under vacuum at room temperature almost always resulted in highest scores. Thus, while a low humidity sample stored in air for 16 weeks gave very high flavor scores, these scores were still better in identical samples stored in vacuum.

4) Taste scores were similar for samples consumed either dry or rehydrated, though it was noted that rehydration tends to result in improvement of samples of lower taste scores, most likely due to reduction of the intensity of off-flavors due to dilution in rehydration water.

5) The general trends observed in storage, which are noted in 1-4 above, are the same for sucrose and maltodextrin samples. As has been often noted, however, the sucrose treated samples generally have higher scores and this advantage is retained during storage for samples of low water activity.

Based on these observations, it will be necessary to insure that peach slices are freeze dried to a low moisture level and packaged in a low humidity environment. Packaging should be in a material of low water permeability. Vacuum packaging (or perhaps nitrogen flushing) would be

advantageous but does not appear to be essential with respect to flavor or texture quality. If the product is maintained dry, it seems that storage at normal ambient conditions will give a highly acceptable product.

Apple Slices - The storage study using freeze dried apple slices has been initiated. Of particular interest will be an evaluation if improved storage stability results from vacuum packing for this product.

Table 1

Results of Organoleptic Evaluation of Blanched or Unblanched Osmotic Pretreated Apples

	Difference Test	
	Taste	Texture
Blanched IS	4.08	4.25
Unblanched IS	3.83	4.08
NS	3.67	3.67

Taste: NSD
Texture: blanched IS/NS 5%

	Preference Test	
Blanched IS/Unblanched IS	8/12	NSD
Unblanched IS/NS	9/12	NSD
Blanched IS/NS	8/12	NSD

	Ranking Test	
First	Blanched IS	.283
Second	Unblanched IS	0
Third	NS	-.283

NSD = no significant difference

Table 2

Average sample scores for organoleptic tests

(For codes see text)

Sample	Fruit	Taste	Texture
1	Cherries		
	NS	3.36	3.54
	NF	3.29	2.79
	IS	3.18	3.32
	IF	3.00	2.71
2	Honeydew		
	NS	3.63	3.70
	NF	3.13	3.33
	IS	3.63	3.37
	IF	3.27	2.67
3	Cantaloupe		
	NS	3.92	3.88
	NF	4.00	4.00
	IS	4.77	3.92
	IF	4.08	3.23
4	Strawberries		
	NS	4.21	3.61
	NF	3.57	3.86
	IS	3.93	4.50
	IF	3.79	3.50
5	Cantaloupe		
	NS	3.84	4.05
	NF	--	--
	IS	4.50	3.97
	IF	3.95	3.11
6	Strawberries		
	NS	3.79	3.58
	NF	3.42	3.07
	IS	4.42	4.21
	IF	4.12	3.46

Table 2 continued

Sample	Fruit	Taste	Texture
7	Cantaloupe (rehydrated)		
	NS	3.29	-
	NF	2.50	-
	IS	3.42	-
	IF	2.92	-
8	Pears		
	NS	3.90	3.35
	NF	3.90	3.90
	IS	4.65	4.35
	IF	3.60	3.80
9	Peaches		
	NS	2.83	3.00
	NF	2.42	2.83
	IS	4.25	4.42
	IF	3.50	3.17
10	Pineapple		
	NS	3.50	4.05
	NF	2.42	3.36
	IS	4.37	4.05
	IF	3.75	3.45
11	Pears		
	NS	3.55	3.55
	NF	4.20	4.30
	IS	4.58	3.80
	IF	3.10	2.30
12	Apples		
	NS	2.62	3.25
	NF	2.58	2.87
	IS	4.58	4.67
	IF	3.75	3.17
13	Apples (rehydrated)		
	NS	2.85	-
	IS	4.69	-
	IF	4.00	-

Table 2 continued

Sample	Fruit	Taste	Texture
14	Apples		
	IS	4.00	3.85
	IS*	4.46	4.23
	NS	3.31	2.92
	(*heated 2 hrs at 80° C)		
15	Apples		
	IS	4.07	3.71
	IVS	4.21	3.36
	NS	3.36	3.21
16	Apples		
	IS	4.31	3.69
	MIS	3.00	3.19
	NS	3.06	2.13
17	Peaches		
	IS	3.36	3.36
	MIS	3.00	2.91
	NS	3.64	3.36
18	Cantaloupe		
	IS	4.38	3.77
	MIS	3.69	3.31
	NS	3.62	3.15
19	Cantaloupe		
	IS	4.00	3.82
	MIVS	4.45	3.27
	NS	3.55	3.64
20	Strawberries		
	IS	4.33	4.17
	MIVS	3.00	3.08
	NS	3.50	3.08
21	Strawberries (rehydrated)		
	IS	4.17	-
	MIVS	3.33	-
	NS	3.67	-
22	Peaches		
	IS	3.36	2.45
	MIVS	3.55	3.55
	NS	2.36	2.64

Table 2 continued

Sample	Fruit	Taste	Texture
23	Strawberries (rehydrated)		
	IS	4.15	-
	MIVS	3.85	-
	NS	3.31	-
24	Peaches		
	IS	4.67	4.33
	MIS	3.50	3.33
	NS	3.08	2.58
25	Peaches		
	IS	4.08	4.17
	IVS	3.88	3.58
	NS	3.75	3.50
26	Peaches (rehydrated)		
	IS	4.23	-
	IVS	3.00	-
	NS	3.54	-
27	Peaches		
	MIVS	4.08	3.75
	IVS	3.83	4.00
	NS	3.67	3.33
28	Peaches		
	IS (3 hrs)	4.00	3.83
	IS (5 hrs)	3.75	3.83
	NS	3.75	2.92
29	Pineapple		
	NS	4.50	4.42
	IS	3.92	3.42
	MIS	3.50	4.17
30	Pineapple		
	NS	4.15	4.23
	MIVS	3.85	3.85
	MIS	2.54	2.31

Table 3

Sample Scores for Ranking Tests

(For codes see text)

Sample #	Fruit	Rank			
		First	Second	Third	Fourth
1	Cherries	NS .190	IS .180	IF .130	NF -.140
2	Honeydew	NS .300	IS .260	NF -.037	IF -.530
3	Cantaloupe	IS .675	NS .023	NF -.274	IF -.406
4	Strawberries	IS .380	NS .095	NF -.095	IF -.380
5	Cantaloupe	IS .492	NS -.224	IF -.268	-
6	Strawberries	IS .737	NS .161	IF -.211	NF -.687
7	Cantaloupe (rehydrated)	IS .333	NS .122	IF 0	NF -.454
8	Pears	IS .678	NF -.060	NS -.206	IF -.412
9	Peaches	IS .969	IF -.001	NS -.233	NF -.726
10	Pineapple	IS .687	IF .172	NS .111	NF -.926
11	Pears	NF .618	IS .326	NS -.266	IF -.678
12	Apples	IS 1.03	IF .250	NF -.518	NS -.787
13	No test conducted on Sample 13				

Table 3 (continued)

Sample #	Fruit	First	Second	Third
14	Apples	IS .390	IS[a] .330	NS -.720
15	Apples	IS .243	IVS .243	NS -.488
16	Apples	IS .530	MIS 0	NS -.530
17	Peaches	IS .142	NS 0	MIS -.142
18	Cantaloupe	IS .392	MIS -.131	NS -.262
19	Cantaloupe	MIVS .077	IS 0	NS -.077
20	Strawberries	IS .638	MIVS -.213	NS -.425
21	Strawberries (rehydrated)	IS .567	MIVS -.043	NS -.142
22	Peaches	MIVS .618	IS -.077	NS -.541
23	Strawberries (rehydrated)	IS .262	MIVS .196	NS -.458
24	Peaches	IS .708	MIS -.213	NS -.456
25	Peaches	IS .283	IVS 0	NS -.283
26	Peaches (rehydrated)	IS .458	NS -.196	IVS -.262
27	Peaches	IVS .283	MIVS 0	NS -.283
28	Peaches	IS(3) .283	IS(5) .071	NS -.354
29	Pineapple	NS .354	MIS -.142	IS -.213
30	Pineapple	NS .458	MIVS .196	MIS -.654

a) IS sample heated 2 hrs at 80°C in dry state

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Table 4

Summarized significant results for organcleptic tests of freeze dried fruits

(see text for codes)

Sample		Difference Test		Preference Test			Ranking Test	
		Taste	Texture	Preference*		Significance	(preferred is first)	
1	Cherries	NSD	IF/NS 5% NF/NS 5%	SN/NF NS/IS IS/IF	8/14 8/14 10/14	NSD NSD NSD	NSD	
2	Honeydew	NSD	IF/NS 1% IF/IS 5% IF/NF 5%	IS/IF NS/NF IS/NS	13/15 11/15 8/15	1% NSD NSD	IS/IF NS/IF	1% 1%
3	Cantaloupe	NS/IS 1% IF/NF 5% IS/IF 5%	IF/NF 5%	IS/IF IS/NS NS/NF	11/13 11/13 7/13	5% 5% NSD	IS/IF IS/NF IS/NS	1% 1% 5%
4	Strawberries	NSD	IS/IF 5% IF/NF 5% NS/IS 5% IF/NF 5%	IS/IF NS/NF NS/IF	10/14 8/14 8/14	NSD NSD NSD	IS/IF	5%
5	Cantaloupe	IS/NS 5%	NS/IF 1%	IS/NS IS/IF	14/19 15/19	NSD 5%	IS/IF IS/NS	1% 1%
6	Strawberries	NF/IS 1% NF/IF 1% NS/IS 5%	NF/IS 1% IS/IF 5% NS/IS 5%	IS/NS IS/IF NS/NF	10/12 10/12 9/12	5% 5% NSD	IS/NF IS/IF IS/NF IS/NS IF/NF	1% 1% 1% 5% 5%
7	Cantaloupe (rehydrated)	NSD	-	NS/NF IS/NS IS/IF	9/12 8/12 8/12	NSD NSD NSD	IS/NF	5%

Table 4 (continued)

Sample		Difference Test		Preference Test			Ranking Test	
		Taste	Texture	Preference*		Significance	(preferred is first)	
8	Pears	IS/IF 5%	NS/IS 1%	IS/NS	7/10	NSD	IS/IF	1%
				NS/NF	5/10	NSD	IS/NS	1%
				IS/IF	8/10	NSD	IS/NF	5%
9	Peaches	IS/NS 1%	IS/NF 1%	IS/IF	11/12	1%	IS/IF	1%
		IS/NF 1%	IS/NS 1%	NS/NF	9/12	NSD	IS/NS	1%
		IF/NF 1%	IS/IF 1%	IS/NS	12/12	0.1%	IS/NF	1%
		IF/NS 5%					IF/NF	1%
		IS/IF 5%					NS/NF	5%
10	Pineapple	NF/NS 1%	NSD	IS/IF	8/12	NSD	IS/NS	1%
		NF/IF 1%		IS/NS	7/12	NSD	IS/NF	1%
		NF/IS 1%		IS/NF	11/12	1%	IF/NF	1%
		IS/NS 5%					NS/NF	1%
							IS/IF	5%
11	Pears	NF/IF 1%	NF/IF 1%	NF/NS	8/10	NSD	NF/IF	1%
			NF/IS 1%	IS/NS	8/10	NSD	NF/NS	1%
			NF/NS 1%	IS/IF	9/10	5%	IS/IF	1%
							IS/NS	5%
12	Apples	IS/NF 1%	IS/NS 1%	IS/IF	12/12	0.1%	IS/NS	1%
		IS/NS 1%	IS/IF 1%	NF/NS	8/12	NSD	IS/IF	1%
		IF/NF 1%	IS/NF 1%	IS/NS	12/12	0.1%	IS/NF	1%
		NS/IF 1%					IF/NS	1%
		IS/IF 1%					IF/NF	1%
							NS/NF	5%
13	Apples (rehydrated)	NS/IS 1%	-	IS/NS	13/13	0.1%		
		NS/IF 1%		IS/IF	12/13	1%		
		IS/IF 5%						

Table 4 (continued)

Sample	Difference Test				Preference Test			Ranking Test	
	Taste		Texture		Preference*		Significance	(preferred is first)	
14 Apples (a-heated in dry state for 2 hrs at 80°C)	IS/NS	5%	IS/NS IS[a]/NS	1% 5%	IS[a]/IS IS/NS	7/13 12/13	NSD 1%	IS/NS IS[a]/NS	1% 1%
15 Apples	IS/NS IVS/NS	5% 5%	NSD		IVS/NS IS/NS IVS/IS	11/14 11/14 7/14	NSD NSD NSD	IS/NS IVS/NS	1% 1%
16 Apples	IS/MIS IS/NS	1% 1%	IS/NS MIS/NS	1% 5%	MIS/NS IS/MIS IS/NS	11/16 13/16 14/16	NSD 5% 1%	IS/MIS MIS/NS IS/NS	5% 5% 1%
17 Peaches	NSD		NSD		NS/MIS IS/MIS IS/NS	7/12 9/12 7/12	NSD NSD NSD		NSD
18 Cantaloupe	IS/NS	5%	IS/NS	5%	IS/NS IS/MIS MIS/NS	9/13 10/13 8/13	NSD NSD NSD	IS/NS	5%
19 Cantaloupe	MIVS/NS	5%	IS/MIVS IS/NS	1% 1%	IS/MIVS MIVS/NS NS/IS	6/11 6/11 6/11	NSD		NSD
20 Strawberries	IS/MIVS IS/NS	1% 5%	IS/NS IS/MIVS	1% 1%	MIVS/NS IS/NS IS/MIVS	6/12 11/12 11/12	NSD 1% 1%	IS/MIVS IS/NS	1% 1%
21 Strawberries (rehydrated)	Too few samples for significance				IS/MIVS IS/NS NS/MIVS	4/6 5/6 5/6	Too few samples for significance	Too few samples for significance	
22 Peaches	MIVS/NS IS/NS	1% 1%	MIVS/IS MIVS/NS	5% 5%	MIVS/IS MIVS/NS IS/NS	8/12 12/12 8/12	NSD 0.1% NSD	MIVS/IS MIVS/NS	1% 1%

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Table 4 (continued)

Sample	Difference Test				Preference Test			Ranking Test (preferred is first)	
	Taste		Texture		Preference *		Significance		
23 Strawberries	IS/NS	5%	NSD		IS/MIVS	7/13	NSD	IS/NS	5%
					MIVS/NS	10/13	NSD	MIVS/NS	5%
					IS/NS	9/13	NSD		
24 Peaches	IS/NS	1%	IS/NS	1%	IS/MIS	11/12	1%	IS/NS	1%
	IS/MIS	1%	IS/MIS	1%	IS/NS	11/12	1%	IS/MIS	1%
			MIS/NS	5%	MIS/NS	8/12	NSD		
25 Peaches	NSD								
			IS/NS	5%	IS/IVS	7/12	NSD	-	NSD
			IS/IVS	5%	IS/NS	9/12	NSD		
					IVS/NS	6/12	NSD		
26 Peaches (rehydrated)	IS/IVS	1%	-		NS/IVS	8/13	NSD	IS/IVS	5%
					IS/NS	11/13	5%		
					IS/IVS	11/13	5%		
27 Peaches	NSD		IVS/NS	5%	IVS/NS	8/12	NSD	-	NSD
					MIVS/IVS	7/12	NSD		
					MIVS/NS	8/12	NSD		
28 Peaches	NSD		IS(5)/NS	1%	IS(3)/IS(5)	7/12	NSD	-	NSD
			IS(3)/NS	1%	IS(5)/NS	7/12	NSD		
					IS(3)/NS	8/12	NSD		
29 Pineapple	NS/MIS	5%	NS/IS	1%	NS/IS	9/12	NSD	-	NSD
			MIS/IS	5%	MIS/IS	6/12	NSD		
					NS/MIS	8/12	NSD		
30 Pineapple	NS/MIS	5%	NS/MIS	1%	NS/MIVS	8/13	NSD	NS/MIS	1%
	MIS/MIVS	1%	MIS/MIVS	1%	NS/MIS	12/13	1%		
					MIVS/MIS	11/13	5%	MIVS/MIS	1%

* Number of judges preferring a given treatment/total number of judges

Table 5

Program for Evaluation of Storage Stability of Osmotically Pretreated Freeze Dried Peaches

	Time (weeks)				
AW = 0	0	2	4	8	16
4° (Control	x	x	x	x	x
R.T. (22°C)	x	x	x	x	x
37°C			x	x	
22°C (vacuum pack)			x	x	x
AW = 0.11					
R.T. (22°C)	x	x	x	x	
37°C		x	x		
AW = 0.43					
R.T. (22°C)	x	x	x	x	
37°C		x	x		

AW = Water activity

R.T. = Room temperature

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Name ______________________________

Date ______________________________

Product ______________________________

Please evaluate these samples for flavor and texture. Taste test each one. Use the appropriate scale to show your evaluation, checking the point which best describes your feeling about taste, texture and appearance.

YOU MUST READ THIS STATEMENT AND SIGN THE FORM THAT YOU HAVE DONE SO!

1. I have notified the testers if I have any food allergies.

2. I am willingly partaking in this organoleptic evaluation study. I understand that all the samples to be evaluated are composed of foods or FDA approved food grade materials. I understand that to avoid any bias in the evaluation, I may not be told the exact nature of the foods or process variations being tested, and that I have the right to withdraw at any time.

SIGNATURE ______________________________

Code ____

	Taste	Texture	Appearance
Like Extremely	___	___	___
Like Very Much	___	___	___
Like Moderately	___	___	___
Like Slightly	___	___	___
Neither Like nor Dislike	___	___	___
Dislike Slightly	___	___	___
Dislike Moderately	___	___	___
Dislike Very Much	___	___	___
Dislike Extremely	___	___	___

Reasons

Code ____

	Taste	Texture	Appearance
Like Extremely	___	___	___
Like Very Much	___	___	___
Like Moderately	___	___	___
Like Slightly	___	___	___
Neither Like nor Dislike	___	___	___
Dislike Slightly	___	___	___
Dislike Moderately	___	___	___
Dislike Very Much	___	___	___
Dislike Extremely	___	___	___

Reasons

Code ____

	Taste	Texture	Appearance
Like Extremely	___	___	___
Like Very Much	___	___	___
Like Moderately	___	___	___
Like Slightly	___	___	___
Neither Like nor Dislike	___	___	___
Dislike Slightly	___	___	___
Dislike Moderately	___	___	___
Dislike Very Much	___	___	___
Dislike Extremely	___	___	___

Reasons

Table 6

Table 7

Peaches for Storage - Ave. Difference Test Scores

IS	DRY										REHYDRATED				
	TASTE					TEXTURE					TASTE				
C/R.H.	0	2	4	8	16	0	2	4	8	16	0	2	4	8	16
25/vac.[a]	-	-	6.83	7.36	6.10	-	-	7.17	7.27	6.70	-	-	6.17	7.15	7.30
4/0	(5.75	5.75	6.50	6.00	6.50	(6.08	6.33	6.17	6.45	6.60	(5.92	6.58	6.42	6.15	6.80
25/0	(6.50	5.83	5.50	6.82	6.40	(6.17	6.67	6.17	6.82	6.30	(5.92	6.17	6.42	6.77	6.60
37/0	-	-	5.25	5.36	-	-	-	5.17	5.82	-	-	-	5.92	4.85	-
25/10	5.83	5.83	5.58	6.73	-	6.42	6.25	6.83	6.55	-	5.25	6.00	5.58	6.15	-
37/10	-	5.42	5.50	-	-	-	6.42	6.33	-	-	-	5.50	5.25	-	-
25/43	4.25	4.83	3.33	3.55	-	2.42	3.33	2.83	2.73	-	4.25	5.08	5.25	4.15	-
37/43	-	2.92	2.17	-	-	-	2.25	2.17	-	-	-	3.67	2.42	-	-

MIS	0	2	4	8	16	0	2	4	8	16	0	2	4	8	16
25/vac.[a]	-	-	6.27	6.60	6.00	-	-	6.50	5.70	6.27	-	-	5.60	6.18	6.50
4/0	(5.17	5.17	5.91	6.10	5.82	(5.42	5.67	6.10	5.90	6.18	(5.92	5.36	5.20	5.73	5.40
25/0	(5.58	3.67	5.73	5.90	4.82	(6.33	5.00	6.40	5.70	6.00	(6.33	5.27	5.70	5.64	6.00
37/0	-	-	5.00	4.80	-	-	-	5.90	5.30	-	-	-	5.20	5.55	-
25/10	5.75	5.50	6.18	5.40	-	6.17	6.25	6.50	5.50	-	5.58	4.91	4.80	4.73	-
37/10	-	4.42	5.00	-	-	-	5.08	5.20	-	-	-	4.55	5.30	-	-
25/43	4.75	4.08	4.18	4.40	-	4.17	2.58	4.10	3.50	-	5.25	5.82	5.90	6.27	-
37/43	-	2.92	2.73	-	-	-	2.75	3.00	-	-	-	4.09	3.60	-	-

a. examples at 0% R.H. stored in vacuum sealed cans

IS - osmotically treated with 60% sugar for 3 hours
MIS - osmotically treated with 45% malto dextrin for 3 hours

(indicates on 0 weeks the tar samples are in duplicate
(

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Table 8

Ranking Order for Stored Freeze dried Peaches

	Ranking							
	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.
			Sucrose Pretreatment evaluated dry					
wks.								
0	22/10[a]	22/0[b]	22/0[b]	22/43				
2	22/0	4/0	37/10	22/10	22/43	37/43		
4	22/vac.	4/0	22/10	22/0	37/10	37/0	22/43	37/43
8	22/vac.	22/10	22/0	4/0	37/0	22/43		
16	22/vac.	4/0	22/0					
			Sucrose Pretreatment evaluated rehydrated					
wks.								
0	22/0	22/0	22/10	22/43				
2	22/0	4/0	22/10	37/10	22/43	37/43		
4	22/0	4/0	22/vac.	22/10	37/0	22/43	37/10	37/43
8	22/vac.	22/0	22/10	4/0	37/0	22/43		
16	22/vac.	4/0	22/0					
			Maltodextrin Pretreatment evaluated dry					
wks.								
0	22/10	22/0	22/0	22/43				
2	22/10	4/0	37/10	22/0	22/43	37/43		
4	22/vac.	4/0	22/10	22/0	37/0	37/10	22/43	37/43
8	22/vac.	22/0	4/0	22/10	37/0	22/43		
16	22/vac.	4/0	22/0					
			Maltodextrin Pretreatment evaluated rehydrated					
wks.								
0	22/0	22/0	22/43	22/10				
2	22/0	4/0	22/43	22/10	37/10	37/43		
4	22/43	22/0	4/0	37/10	22/vac.	22/10	37/0	37/43
8	22/vac.	22/0	22/43	4/0	37/0	22/10		
16	22/vac.	22/0	4/0					

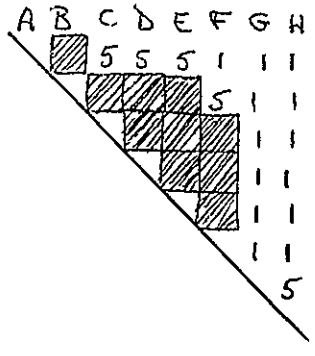
a: Sample code Temperature (°C) / Relative Humidity (%)

b: At zero weeks sample 22/0 evaluated in duplicate

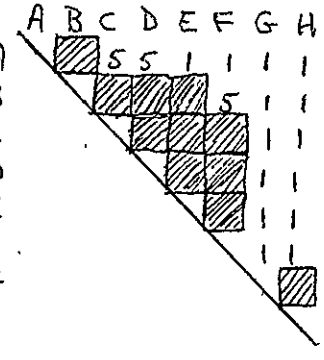
Table 9 Significance of difference of Taste Scores and Ranking Values for Sucrose Treated Peach Slices Stored 4 Weeks

Sucrose Treated - Evaluated Dry

Storage Condition	Taste Score	
22/VAc	6.83	A
4/0	6.50	B
22/10	5.58	C
22/0	5.50	D
37/10	5.50	E
37/0	5.25	F
22/43	3.33	G
37/43	2.17	H

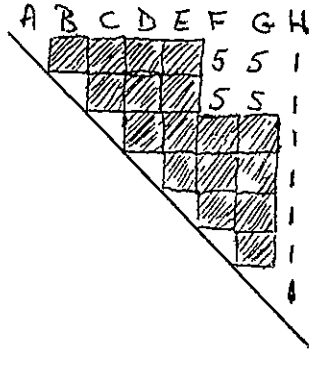


Storage Condition	Rank Score	
22/VAc	.885	A
4/0	.575	B
22/10	.342	C
22/0	.253	D
37/10	.135	E
37/0	.016	F
22/43	-1.01	G
37/43	-1.20	H



Sucrose Treated - Evaluated Rehydrated

Storage Condition	Taste Score	
4/0	6.42	A
22/0	6.42	B
22/VAc	6.17	C
37/0	5.92	D
22/10	5.58	E
37/10	5.25	F
22/43	5.25	G
37/43	2.42	H



Storage Condition	Rank Score	
22/0	.664	A
4/0	.403	B
22/VAc	.393	C
22/10	.135	D
37/0	.045	E
22/43	-.147	F
37/10	-.211	G
37/43	-1.28	H

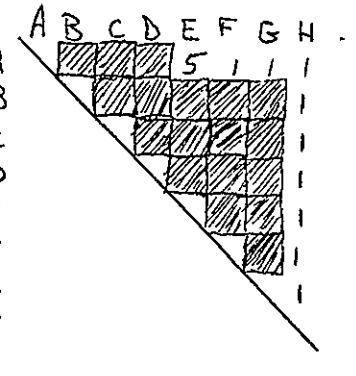
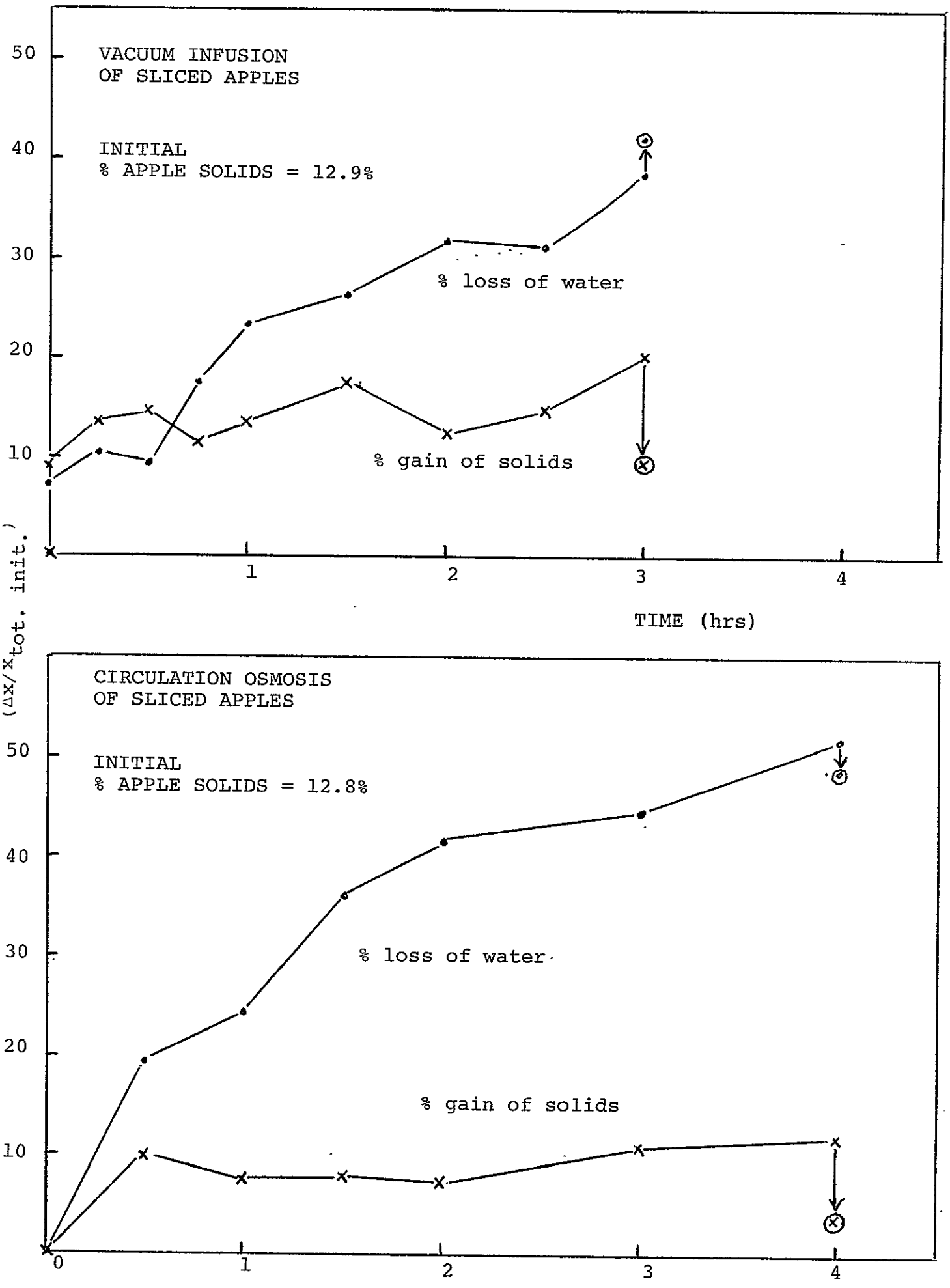


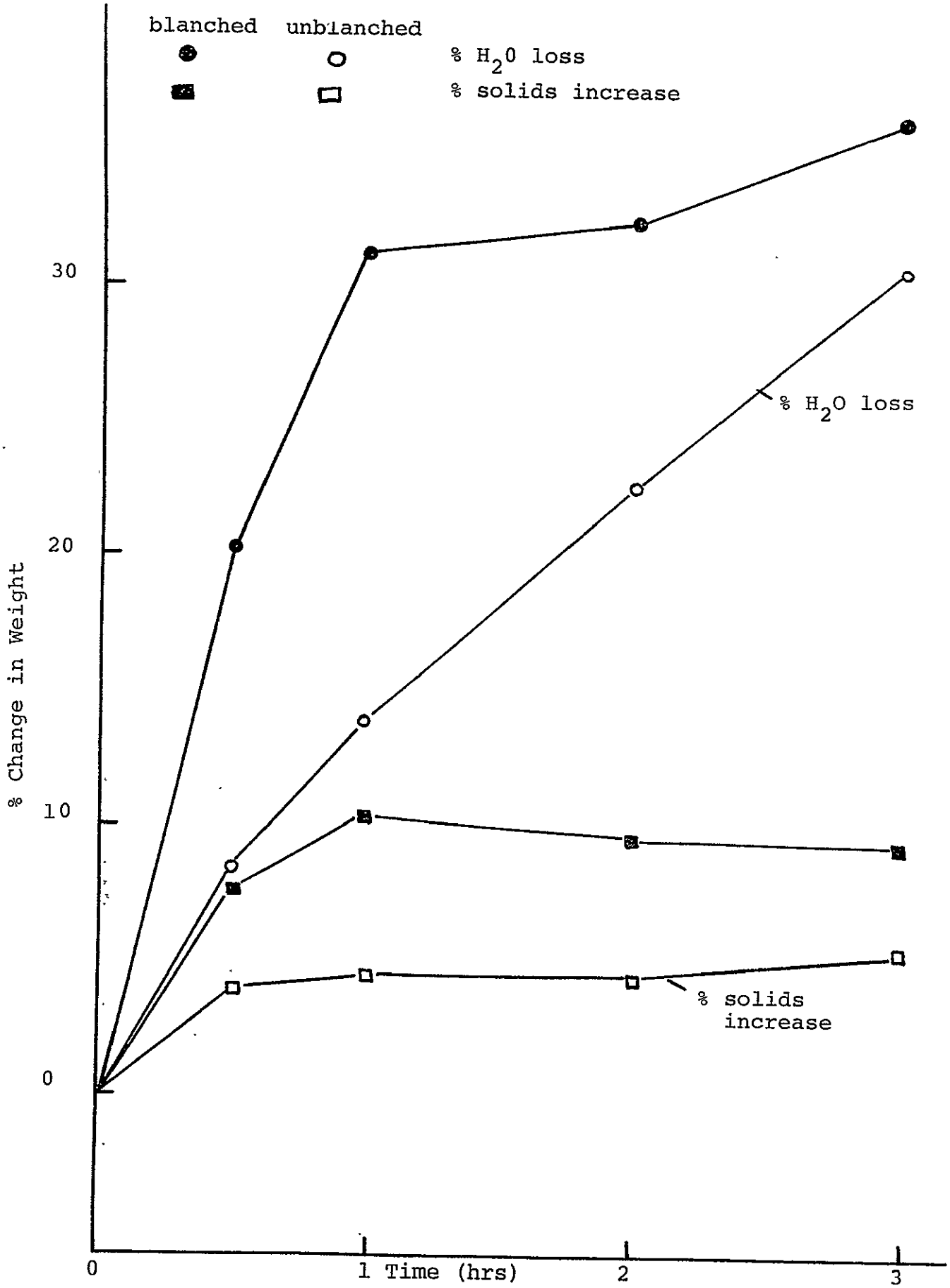
Table 10 Significance of Difference of Organoleptic Tests for Peach Slices Stored 16 Weeks

SAMPLE	TASTE			TEXTURE			RANKING		
	STORAGE CONDITION	TASTE SCORE	SIGNIFICANCE	STORAGE CONDITION	TEXTURE SCORE	SIGNIFICANCE	STORAGE CONDITION	RANK SCORE	SIGNIFICANCE
SUCROSE DRY	4/0	6.50	A	22/VAC	6.70	A	22/VAC	.85	A
	22/0	6.40	B	4/0	6.60	B	4/0	.85	B
	22/VAC	6.10	C	22/0	6.30	C	22/0	-.170	C
SUCROSE REHYDRATED	22/VAC	7.30	A	—			22/VAC	.595	A
	4/0	6.80	B				4/0	-.255	B
	22/0	6.60	C				22/0	-.340	C
MALTODEXTRIN DRY	22/VAC	6.00	A	22/VAC	6.27	A	22/VAC	.232	A
	4/0	5.82	B	4/0	6.18	B	4/0	.155	B
	22/0	4.82	C	22/0	6.00	C	22/0	-.386	C
MALTODEXTRIN REHYDRATED	22/VAC	6.50	A	—			22/VAC	.298	A
	22/0	6.00	B				22/0	.043	B
	4/0	5.40	C				4/0	-.340	C

Figure 1: Kinetics of Osmosis



$(\Delta x/x_{tot.\ init.})$



Water loss and Carbohydrate Uptake during Osmotic Pretreatment of Blanched and Unblanched Apple Slices.

Figure 2

Figure 3: Changes of Taste and Texture Scores for Osmotically Treated Freeze Dried Peach Slices During Storage for 16 Weeks

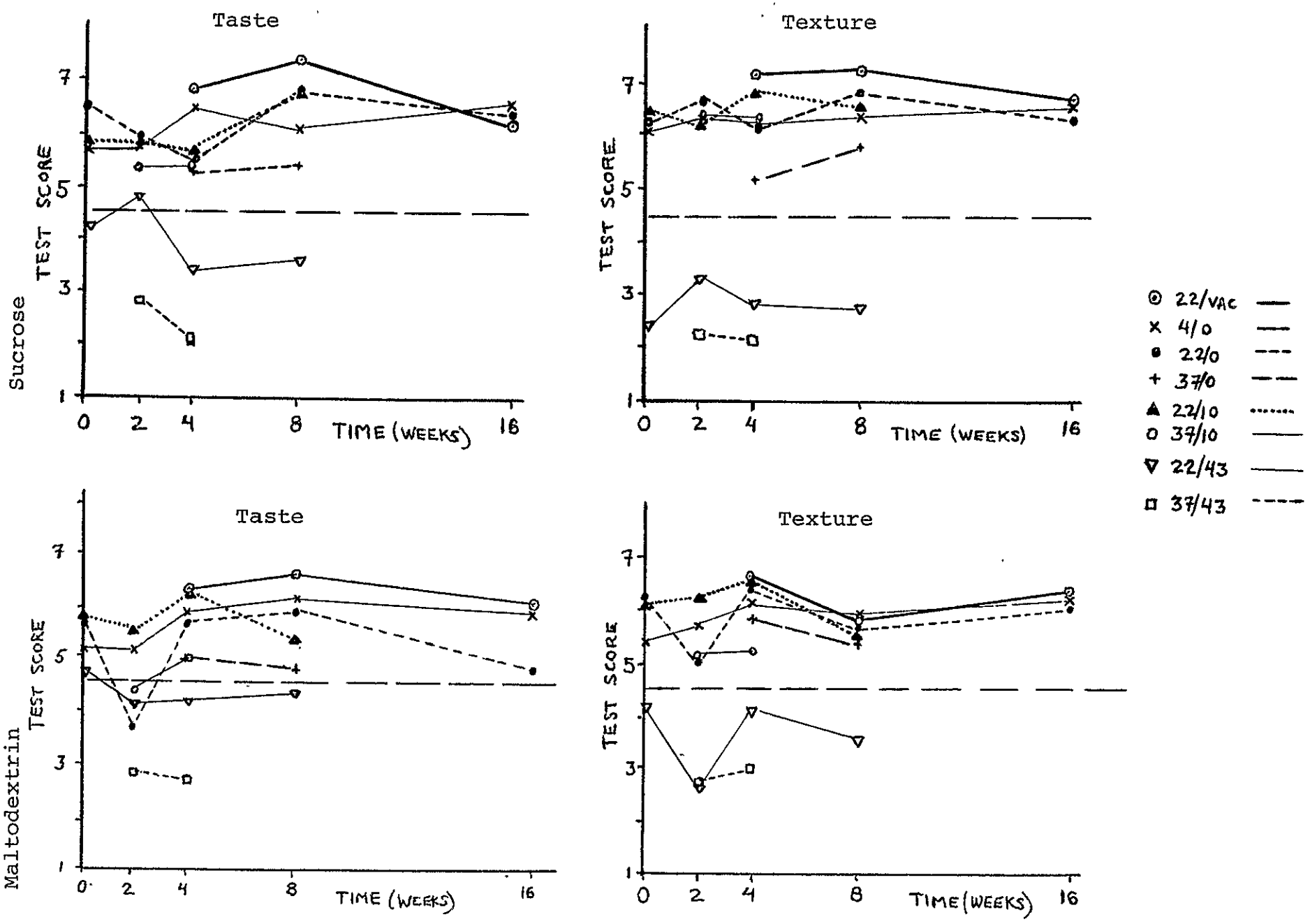
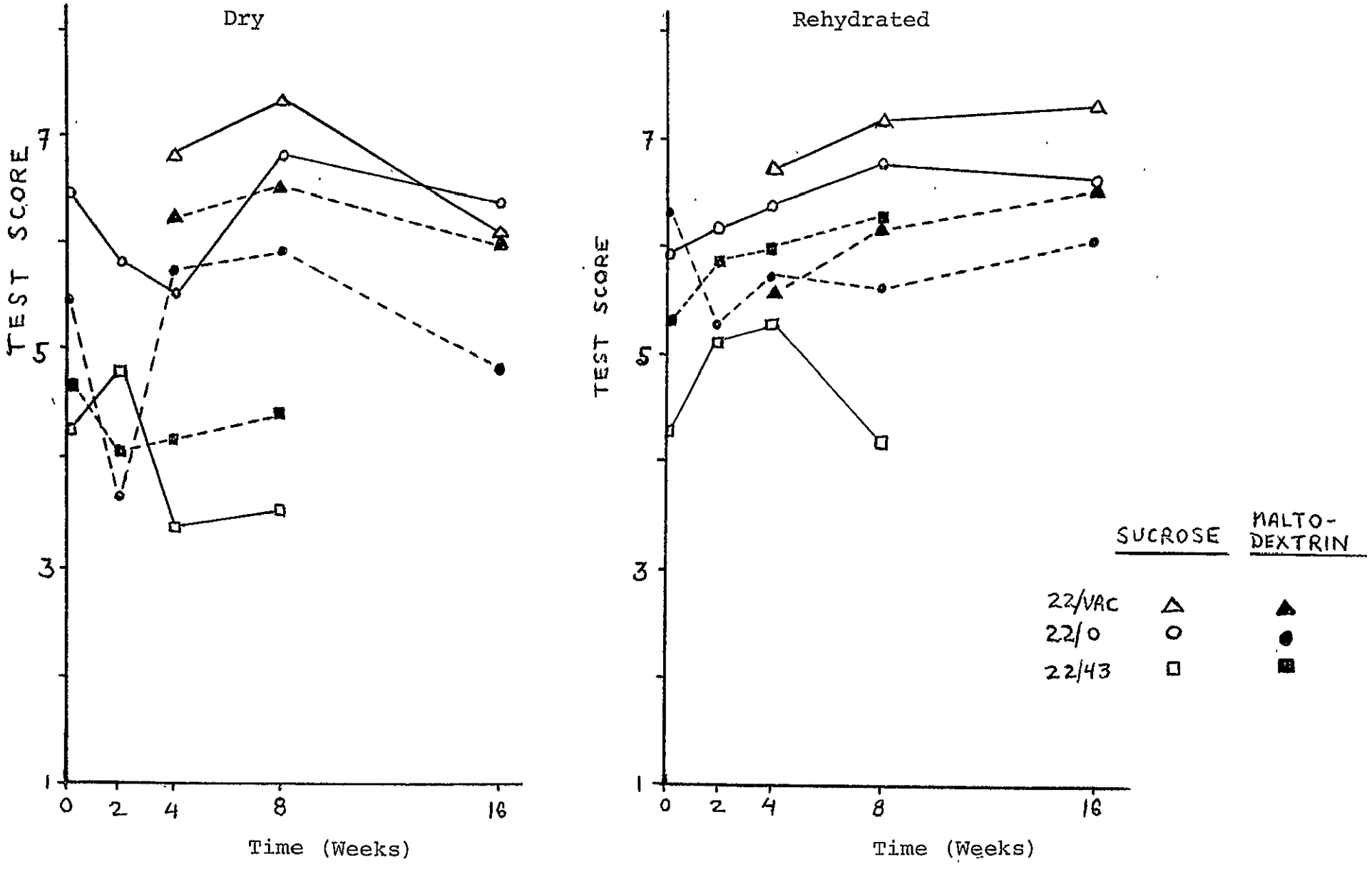


Figure 4: Variation of Taste Scores for Osmotically Treated Freeze Dried Peach Slices Evaluated as Dry and Rehydrated Products



5.5 Manuscript of "Process Conditions for Improved Flavor Quality of Freeze Dried Foods"

Process Conditions for Improved Flavor Quality of Freeze Dried Foods

James M. Flink
Department of Nutrition and Food Science
Massachusetts Institute of Technology
Cambridge, Mass. 02139

Presented at the "Symposium on Flavor Chemistry of Processed Foods", American Chemical Society Meeting, Atlantic City, New Jersey, 9 September 1974

Abstract

Studies on the retention of flavor during freeze drying have been conducted primarily with model systems. These studies have led to the development of some mechanisms by which flavor retention phenomena may be explained and based on these studies, process conditions can be specified so that flavor retention can be optimized. The true worth of these mechanisms rests in their ability to predict processing conditions giving improved flavor quality for real food materials. The present paper reviews the literature and also presents results of studies conducted by the author in which the flavor retention behavior of a number of real food products, including both liquid and solid foods have been evaluated. Among the products considered are coffee, fruit and vegetable juices, and fruits. Process parameters predicted by the mechanisms to be of greatest significance are freezing rate, initial solids content, and conditions which result in maintenance of sample structure (i.e. drying below the collapse temperature). In most cases, flavor quality for the real food showed the same behavior relative to process conditions as predicted by the mechanisms based on model system studies.

Introduction

Freeze drying is generally considered to be the dehydration process which will result in the highest quality dehydrated products. This is due to the fact that water is removed without the presence of a free liquid phase, and that heated regions in the dry layer have low moisture contents, while regions of high moisture have low temperatures. One of the crucial quality aspects, maintenance of product flavor, has aroused much interest in the recent past, as it was felt that flavor components, many of which are highly volatile, would be largely lost during the process since the freeze drying is generally conducted at absolute pressures of below 1 torr.

Most early studies on the retention of flavor during freeze drying have concentrated on simple model systems in which complications due to compositional variations of natural products could be avoided. By means of these studies, in which simple quantitative retention information could be easily evaluated and correlated with changes in process variables, two mechanistic interpretations of flavor retention phenomena during freeze drying were proposed. These were labelled the "selective diffusion" mechanisms (Menting and Hoogstad, 1967; Thijssen and Rulkens, 1968; King and Chandrasekaran, 1973) and the "microregion entrappment" mechanism (Flink and Karel, 1970a) by their respective proponents. These mechanisms have been reviewed

recently by King (1971), Thijssen (1973) and Flink (1973). It appears that there is some agreement that these two proposed mechanisms probably are describing the same basic phenomena from two different approaches, namely mathematical or macroscopic vs. morphological or microscopic viewpoints.

Before presenting some of the results obtained with model systems, it might prove valuable to make the following observations regarding the use of model systems, since to some this may not seem to be a valid approach to determining what will occur in real foods. It has been noted above that natural foods are subject to compositional variations which lead to an undesirable complication regarding analysis of experimental data. Further the number of components which would require monitoring, just to be sure which are varying would greatly increase the experimental burden. Thus model systems were envisioned as serving as simplified versions of real foods, in which compositions were pre-determined and thus well-known. The concentrations of all components were independently variable.

In the present era of food processing, model systems may be considered to serve dual roles since besides modelling real foods they are simplified formulated foods. More and more, foods are being produced by mixing a number of individual ingredients together and processing the mixture. This is precisely the method for producing a model system.

It has sometimes been noted that the concentrations of the model flavor compounds present in the model systems are much higher than concentrations generally shown to be present in real foods, a situation arising from considerations of analytical procedures for the large numbers of samples to be evaluated. While it would seem that data at lower volatile component concentrations would be extremely valuable, the information obtained at the higher concentrations is directly applicable to the freeze drying of preconcentrated feeds, or use of freeze drying to prepare encapsulated flavor concentrates.

In the course of developing mechanisms to explain flavor retention phenomena, a sizeable body of data has been obtained on the influence of process conditions on retention of model flavor compounds in model systems. Only a small fraction of this information can be presented here; more information is available in the articles listed in the bibliography.

Process Conditions and Flavor Retention in Model Systems

A number of processing variables have been investigated, and while the listing below may seem exhaustive, it is likely that there exist others which were unfortunately omitted from this listing. Under each processing variable will be given one or more references from which the information was obtained. It should be emphasized that other references

listed in the bibliography will contain information on one or more of the processing variables.

1. Solids Composition

The influence of the type of solid component on volatile retention has been demonstrated in almost all model system studies published, though direct comparison between studies is hazardous due to the variation of other process parameters. Flink and Karel (1970b) presented a tabulation of the retention of various volatile compounds by a variety of mono-, di- and polysaccharides freeze dried under "identical" conditions. In this case, for most volatiles studied the disaccharides were the most effective, the monosaccharide next, followed by the polymer. In other studies (Chirife and Karel, 1974a) proteins were shown to be effective solids for retention of volatile components.

Studies on binary solid systems at a fixed total solids concentration have shown variable results (Ofcarcik and Burns, 1974; Flink, 1970). For some mixtures retention has improved in a synergistic manner, while in others no effects are noted. It seems likely that this variable behavior is related to the influence of the substituted species on the resultant structural stability of the freeze drying matrix ("collapse"). Thijssen (1972) has shown how the retention of propanol decreases as glucose is substituted for maltodextrin when freeze drying at an ice front temperature of -25°C.

Synergistic effects may result from changes in matrix properties if freezing results in different phase structures of the matrix. Gejl-Hansen (1971) observed freeze dried mixed maltose/maltodextrin systems microscopically. At intermediate levels of maltose substitution, the "dendritic" matrix structure changed to a "cubic cellular" appearance, thought eventually, at higher levels of maltose substitution, the dendritic structure reappeared. Unfortunately, volatile retention behavior was not evaluated.

2. Solids Concentration

Manipulation of the solids concentration can be evaluated in two manners, the percentage retention of the initial volatile, or as the retention of volatile per unit weight of solid. These two methods which are of value for different purposes, will give different interpretations. In the discussion which follows, the percentage retention of initial volatile will be used, since that value is most reported in the literature.

Many researchers have noted the importance of the initial solids concentration on the retention of volatile compounds during freeze drying. Chirife et al (1973) and Thijssen (1973) have presented information showing that, at low solids concentrations (below 10-20%), increases in solids concentration greatly increases volatile retention. When the initial solids concentration is greater than about 25%, there is little effect of further increases on volatile

retention. The initial solids concentration at which volatile retention attains its asymtotic value appears to depend on the volatile species and solid species present in the model system.

If the above observations are considered on a unit weight of solids basis, it is seen that there exists an optimum solids concentration at which the volatile retained per unit of solids is a maximum. This optimum will be lower than the solids concentration at which the volatile retention reaches its asymptote.

3. Initial Volatile Concentration

Similar considerations as noted above relative to method of evaluation must be made. While it has become customary to present volatile retention as a percentage of the initial volatile content, it should be recognized that, for a fixed solids concentration, it is possible that as the initial volatile concentration increases, the percentage volatile retention can decrease while the absolute amount of volatile retained is increasing (and thus the volatile per unit of solids is also increasing). This is shown in Table 1 using the data of Chirife et al (1973). Based on this evaluation, it is difficult to say if the volatile retention has decreased or increased.

Over the range of concentrations most often studied (initial volatile concentration below 1%), it appears that

the percentage retention is relatively constant until low concentrations (100-1000 ppm) are reached, at which point the retention increases.

It should be noted that an opposite effect is reported by Voilley et al (1973) in that increases of initial volatile concentration result in increases in percentage retention.

4. Freezing Rate

The rate of freezing will influence the structure of the freeze dried material as it controls the size of the ice crystals and the degree of solute concentration achieved in the matrix phase. The rate of freezing is one of the most investigated process variables and it can be noted that in all cases reported, slow freezing results in improved retention of the volatile components. The improvements in volatile retention which depend on the retention levels have been reported for the most part to be 2 to 3x (i.e. if rapid freezing gives 20% retention, slow freezing would give 40-60% retention) (Chirife and Karel, 1974).

5. Drying Rate

The rate of freeze drying can be varied in a number of ways, for example by increasing the ice front temperature to improve mass transfer or by increasing the heating plate temperature to improve heat transfer. These changes can be expected to influence volatile retention by means other than just drying rate. In any case, Thijssen (1971) calculated

the effect of drying rates on volatile retention and showed that higher retentions resulted with rapid drying. This was experimentally demonstrated by Rulkens and Thijssen (1972) by maintaining the ice front temperature constant while heating through the frozen layer and controlling the rate of drying by manipulation of the chamber pressure. As an example, drying at chamber pressures giving a doubling of the drying rate at an ice front temperature of -20°C resulted in an increase in n-propanol retention from 65% (slow drying) to 80% (rapid drying). The observed results are sensitive to volatile species, and ice front temperature.

6. Sample Dimensions

The influence of the sample dimensions has been reported for slabs (Chirife et al, 1973a) and for layers of granules (Thijssen, 1974). Sample dimensions which result in improvements in drying rate (thinner slabs or thinner layers of granules) generally will give increased retention of the volatile.

The relationship of diameter of the individual granule to volatile retention is more complex, as there exists for any layer thickness a granule size at which volatile retention is optimum, even though drying rates decrease as the granule size increase (Rulkens and Thijssen, 1972). Since the optimal granule size increases as the freezing rate decreases, it appears that for small particles there

is a relationship of total granule dimension and ice crystal dimension which is important relative to volatile retention.

7. Frozen Layer Temperature and Collapse

The influence of frozen layer temperature has already been alluded to above. Thijssen (1972) and Voilley et al (1973) have shown that as the ice front temperature increases, the retention of volatile compounds decreases. Increases in ice front temperature which do not result in collapse of the drying matrix will nevertheless result, according to the phase diagram, in a decrease of the matrix solids concentration due to the melting of some of the ice crystals.

Collapse is a phenomena in which the matrix undergoes structural degradation due to the onset of viscous flow. Collapse of the freeze drying matrix results in substantial loss of the volatile components, with the loss being directly related to the extent of collapse (Bellows and King, 1973).

8. Heat Input Conditons

Heat input to the sample will influence a number of factors, such as drying rate, temperature gradients, ice front temperature, etc. It has already been shown that drying rate will influence the retention of volatile compounds. Rulkens and Thijssen (1972) have shown that, if the ice front temperature is maintained constant, heating through the dry layer or through the frozen layer

results in equal drying rates and equal retention of volatiles. This indicates that the dry layer temperatures attained during the radiant heat transfer through the dry layer have no effect on the retention of volatile compounds. This effect is not unexpected, based on the results presented by Chirife and Karel (1974b) for heat stability of freeze dried carbohydrates.

When considering the effects of heating conditions, in which heat input is not controlled so as to maintain a constant ice front temperature, the possibility for increased loss of volatile occurs, especially if some collapse occurs. The contradictory retention behavior exhibited by various carbohydrates when heated at different heating platen temperatures (ice front temperatures were not monitored) as presented by Flink and Karel (1970b), is presumably due to the increasing extent of collapse in the glucose samples nulifying any improvement due to increased drying rate, while the non-collapsing sample (dextran) shows an increase in volatile.

9. Summary of Model System Studies

Based on the volatile retention behavior observed in freeze drying model systems, it is seen that on a percentage retention basis the most important processing variable are:

1) Ice Front Temperature
2) Freezing Rate
3) Solids Concentration.

Processing Conditions and Flavor Retention in "Real" Foods

This section will be divided into two parts, one being short summaries of literature articles having flavor retention data for real foods, and the other being a more comprehensive presentation of two studies which have not been previously reported in the technical literature.

1. Apple Juice (Chandrasekaran and King, 1971): Apple juice was freeze dried for a period of time which gave partial removal of the initial water (i.e. the material was not dry when the experiments were halted, still containing about 80% of the initial water). They observed that while the eutectic melting point is about -23°C, the samples begin to show surface liquid at temperatures of -26°C, thus causing termination of the drying. Four major regions of the vapor phase gas chromatogram were evaluated for flavor retention. In all cases, the volatile retention behavior improved as the initial solids content of the apple juice was increased from 17 to 36%. A further increase in solids to 44% showed no improvement over the retention at 36% solids. At the time of termination of the experiments, volatiles retentions were determined to be:

	Flavor Retention (%)			
	Solids Content			
	17%[a]	26%	36%	44%
Ethyl Acetate Region	78	74	75	80
n-Hexanal Region	61	60	73	70
2-Hexenal Region	66	65	80	78
n-Hexyl Acetate Region	50	50	70	70

a only 10% of initial water removed

2. Apple slices (Saravacos and Moyer, 1968): Freeze dried apple slices were reconstituted in water containing 4 volatile organic compounds and then re-freeze dried. The apple slices showed retention behavior very similar to that exhibited by low methoxy pectin gels, with retention levels dependent on the volatile species being considered.

3. Apricots (Lee et al, 1966a): In a comparison of various methods for drying apricots, freeze drying was conducted using either slow (cabinet at -25°C) or rapid (liquid nitrogen immersion) as the freezing treatment. Retention of flavor did not vary with freezing treatment and was approximately 91% as measured by volatile reducing substances and 93% as measured by volatile carbonyl compounds. Histological comparison of the fresh apricots and the two freeze dried samples showed that the liquid nitrogen frozen and dried samples had a cell structure almost unchanged from the fresh, while the slow frozen sample showed a disrupted cell structure due to ice crystal growth. It appears that this cellular disruption has no effect on flavor retention.

4. Banana Puree (Flink, 1970): The influence of addition of sugar (16%) to banana puree on the retention of volatiles was noted in some preliminary thesis experiments. The results of these experiments showed that the more volatile components were retained to a lower extent,

that sugar addition had a greater effect on the less volatile species, (2-pentanone and butanol) than on the more volatile species (ethanol, ethyl acetate, isobutylacetate and isoamyl acetate), and that flavor retention data was more variable when samples had added sugar.

5. Coffee (Ettrup-Petersen et al, 1973): The influence of various freezing procedures (both rates and gas incorporation) and chamber pressures (ice front temperatures) were investigated for their effect on retention of flavor during freeze drying of coffee granules (Table 2). The retention of flavor was improved by slow freezing and by freeze drying at the lowest ice front temperature. The influence of gas addition was dependent on the method used for incorporation. It was further demonstrated that sizable loss of flavor occurs when the ice front temperature is allowed to reach the collapse temperature.

(Hair and Strang, 1969): The time-temperature tolerance of the dry layer to flavor changes was presented for conditions designed to give "no noticable flavor loss" or "no significant flavor loss". With an ice front temperature of -25°C, the dry layer should not be permitted above 93°C. Some examples of maximum times at various temperatures are given below:

Temperature (°C)	Time at given temperature (hr)	
	No noticeable flavor loss	No significant flavor loss
40	3.75	7.5
60	2.25	4.5
80	1.5	2.5

6. Onion Juice (Ofcarcik and Burns, 1974): Pyruvic acid retention was determined for Bermuda onion juice with added carbohydrates, or with added mixtures of carbohydrates. They showed that addition of glucose, sucrose or lactose gave improved retention up to 10% added solids; addition above this concentration gave very little improvement in pyruvic acid retention. When mixtures of sugars at a total solids concentration of 10% are added to the onion juice, no effect of added sugar composition was noted.

7. Orange Juice (Voilley et al, 1973): Retention of a number of flavor compounds was determined for natural orange juice, dearomatized orange juice with added volatiles, and a model solution with added volatiles. When the added volatiles were present initially at either 1000 or 100 ppm, in the dearomatized juice, the percentage retention was the same. This contrasts with the behavior observed for the model system where they found that the percentage retention decreased as the initial volatile concentration decreased. The natural juice showed retention behavior similar to that observed with the dearomatized juice. Some typical results are shown below:

	% retention				
	Natural juice	Dearomatized juice		Model solution	
		100 ppm	1000 ppm	100 ppm	1000 ppm
Ethanol	31	34	29	22	27
Butanol	-	51	47	27	48
Pentanol	-	52	56	31	34
Limonene	63	64	63	-	-

(Massaldi and King, 1974b): Measurements of d-limonene retention for freeze dried orange juice showed an apparent influence of d-limonene solubility and subsequent stabilization of the insoluble d-limonene droplets by "cloud particles". With increasing initial d-limonene content, samples with cloud showed improved retention while samples without cloud had sizable decreases in retention.

(Berry and Froscher, 1969): The retention of d-limonene and water soluble volatiles was investigated as a function of initial d-limonene concentration and freeze dryer heating plate temperature. A summary of their results is presented below:

	Retention (%)		
Heating plate temperature (°F)	d-limonene initial concentration		Water soluble volatiles
	0.011%	0.046%	
120	26	30	22
110	48	30	28
100	54	26	24
90	26	42	19
80	29	30	24
70	44	-	24

It appears that for each volatile, there is some optimal heating plate temperature, though in some cases the variation is not too great.

(Sauvageot et al, 1969): The influence of a variety of process variables on the retention of a number of flavor compounds of orange juice and raspberry juice is summarized in Table 3. These results conform with few exceptions to those noted with model systems.

8. Peaches (Lee et al, 1966b): Peach slices were freeze dried following fast freezing (liquid nitrogen immersion), slow freezing (cabinet at -25°C) and partial osmosis followed by slow freezing. The retention of volatiles, which was measured as volatile reducing substances and volatile carbonyl compounds is presented below:

Treatment	Soluble solids content(%)	Volatile reducing substances	Volatile carbonyls
Fast freezing	11.0	98	92
Slow freezing	11.6	94	92
Partial osmosis & slow freezing	17.0	103	127

It can be seen that freezing rate had little effect on retention of the volatile compounds. The authors postulate that the greater than 100% retention with the osmotic treatment may result from fragmentation of reducing sugar during dehydration.

9. Raspberry Juice (Sauvageot et al, 1969): The influence of a variety of process variables on the retention of a number of flavor compounds of raspberry juice is summarized in Table 3 (This is the same table as noted in 7. above).

The remainder of this paper will present results of two previously unpublished studies on flavor retention in tomato juice and fruit slices.

Tomato Juice: Retention of flavor compounds in freeze dried tomato juice: In a study conducted by Mr. Mogens Granborg at the Food Technology Laboratory of the Technical University of Denmark while this author was a Guest Professor at that institution, the influence of a number of process variables on retention of flavor compounds of tomato juice was investigated.

In the first part of the study, 3 alcohols (ethanol, propanol and butanol, each at 0.1% w/v) were added to canned tomato juice having a solids concentration of 7%. The results are presented in Table 4. A number of observations of interest can be noted. The most striking improvement in retention of flavor results from increasing the sample thickness, a finding quite to the contrary of those noted in model system studies. This might, however, be due to slower freezing of the thicker samples. In agreement with model system studies, the slower the freezing

rates, the better the retention. Lastly, in almost all cases, the retention increases with increasing number of carbons in the volatile molecule. In one case, a comparison of retentions in 10 mm thick samples frozen by the step program was conducted for volatiles at initial concentrations of either 0.1% or 0.01% each. The results, shown below, indicate that retention was higher at the higher initial alcohol concentration.

	% Retention		
Initial alcohol concentration (%)	Ethanol	Propanol	Butanol
0.1	52	62	62
0.01	39	40	41

Fruit Slices: In model system studies, it was demonstrated that product flavor quality depended primarily on the initial solids content and rate of freezing, if freeze drying was conducted so that matrix structural changes were avoided. In recent studies, experiments were conducted to determine if these same processing variables were significant in determining flavor quality of solid foods.

The initial solids content was increased by an osmotic pretreatment. Sliced fruit was placed in a stirred 60% sucrose solution for a period of up to 6 hours. During this period water was lost by the fruit tissue due to differences in osmotic pressure. Some sugar was taken

up by the surfaces of the fruit, but most was removed by a short (30 sec) rinse prior to freezing. The rinse was necessary to prevent stickiness of the dehydrated product. Table 5 gives the increase of initial solids concentration for a number of the fruits listed. In almost all cases, the contribution of added sugar is about 4%.

Samples were either slowly frozen in a -20°C chamber or rapidly frozen by immersion in liquid nitrogen. All samples were freeze dried under identical conditions.

The four samples produced were encoded as noted below:

IS increased solids, slow frozen

IF increased solids, fast frozen

NS normal solids, slow frozen

NF normal solids, fast frozen

Three methods of organoleptic testing were utilized in evaluating the relative quality of the different processing conditions for a number of fruit products.

Products were scored in a difference test for taste and texture using the following scale (together with numerical equivalents): very poor (1), poor (2), fair (3), good (4), very good (5) and excellent (6). By analysis of variance, the differences between samples were evaluated for significance. In addition, the average value of the scores can be used as a measure of product acceptability.

A second test was a paired comparison preference test in which samples were presented in groups of two. In this case, the judge merely expresses a preference for one sample over the other. By consideration of the various

combinations of paried comparisons, an overall preference can be determined.

In the third organoleptic test, all samples were presented for ranking according to overall quality. By analysis of variance an evaluation of ranking significance can be made. For most tests, when four samples were presented, the degree to which the sample score approaches +1.03 is a measure of its overall acceptance and the difference between values is a measure of the degree of preference.

The results of the organoleptic evaluations are presented in a series of Tables (6-9).

The scores of the difference tests are presented in Table 6, and numerical evaluations of ranking preference tests in Table 7. The highest scores for taste are given in almost all cases to the increased solids, slow frozen (IS) fruits. The notable exception is with cherries where all the samples have a "fair" rating. In most cases, the IS fruits have rated above 4.0 for taste, with a number of samples in the "very good" range (above 4.5). The ranking preference tests (Table 6) also demonstrate the clear superiority of the IS fruits. Evaluations of statistical significance of the various organoleptic tests are

shown in Table 8 these being summarized in Table 9. These data demonstrate the superiority of the IS fruits.

Conclusion

It has been shown through studies using model systems and real foods, that the retention of flavor quality during freeze drying is dependent on the process conditions chosen. In most cases, the retention behavior exhibited by the model system studies, and predicted by the currently accepted mechanistic interpretations of freeze drying flavor retention, is also observed with real foods. In particular, the most important process condition appears to be drying so that matrix structure remains unaltered. If this conditions is met, the most important process variables are initial solids content and freezing rate. It has been demonstrated that by proper control of the process parameters, retention of flavor compounds can be increased by factors of 2-3.

Acknowledgement

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Table 1

Retention of n-propanol by PVP[a] following freeze drying

Initial volatile concentration ppm	Volatile retention %	Volatile retained ppm
50	67	33
100	59	59
800	28	224
10,000	26	2600
20,000	25	5000

[a] Initial PVP concentration = 20%

Table 2

Relative retention of coffee volatiles (based on total peak area) for various freezing and freeze-drying conditions

Freezing conditions[a]	Relative retention (%)[b] freeze-drying chamber pressure (torr)						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
very slow	92	96	78	77	66	67	34
slow	100	99	88	82	91	82	35
foam, slow	67	61	49	53	57	44	63
quick	47	53	38	38	44	35	36
foam, quick	48	-	42	42	43	32	29

[a] very slow stepwise to -40°C
slow -40°C
quick spray onto chilled drum at -52°C

[b] relative to slow frozen sample dried at 0.2 torr

From Ettrup-Petersen et al (1973)

Table 3

Generalized summary of results presented by Sauvageot et al (1969)

Process Parameter Increased	Units	Values	General Trend in Retention	Exceptions
Chamber pressure	Torr	0.02 0.12	No change	None
Freezing rate	°C/min	0.5 6.6 16	Decreased retention	A few noted with orange juice
Frozen layer temperature	°C	-26 -36	No change	Ethanol shows large decrease
Temperature during desorption	°C	28 40 60	Raspberry juice: some loss when compare 28°C to 60°C Orange juice: no change between 25°C and 45°C	Acetaldehyde has sizeable decrease
Duration of desorption	hr	9 7	Some decrease especially when dry at -36°C	Acetaldehyde shows no effect
Thickness of frozen layer	mm	5 10	Slight decrease in retention	
Dry solids content	%	12 18	Retention increased	Acetaldehyde shows no change Ethanol decreased

Table 4

Retention of volatile alcohols during freeze drying of tomato juice

Freezing conditions	Retention of Alcohols (%) (Ethanol-Propanol-Butanol) Thickness			
	3 mm	5 mm	7.5 mm	10 mm
-40°C Blast	7-11-14	-	-	41-57-63
-40°C Still Air	15-23-27	27-40-47	39-58-64	40-53-63
Step Program[a]	17-22-22	40-51-56	-	52-62-62

[a] -8,-20,-30,-40 °C

Table 5

Increase in solids concentration due to osmotic pretreatment

	Solids concentration (%)	
Fruit	Before osmosis	After osmosis
Strawberries	9.4	23.0
Honeydew melon	9.6	33.6
Cantoloupe melon	9.6	28.0
Peaches	10.7	29.4
Pears	14.3	28.0
Pineapple	12.1	27.9
Apples	12.8	29.9

Table 6

Sample Scores for Difference Tests for Taste Acceptability

Sample #		Organoleptic Scores[a]			
		IS	IF	NS	NF
1	Cherries	3.18	3.00	3.36	3.29
2	Honeydew	3.63	3.27	3.63	3.13
3	Cantaloupe	4.77	4.08	3.92	4.00
4	Strawberries	3.93	3.79	4.21	3.57
5	Cantaloupe	4.50	3.95	3.84	-
6	Strawberries	4.42	4.12	3.79	3.42
7	Cantaloupe (rehydrated)	3.42	2.92	3.29	2.50
8	Pears	4.65	3.60	3.90	3.90
9	Peaches	4.25	3.50	2.83	2.42
10	Pineapple	4.37	3.75	3.50	2.42
11	Pears	3.75	3.10	3.55	4.20
12	Apples	4.58	3.75	2.62	2.58
13	Apples (rehydrated)	4.69	4.00	2.85	-

[a] 6 = excellent
1 = very poor

Table 7

Sample Scores from Ranking Tests

the extreme values of ranking ±1.03
solids content: N:normal, I:increased
freezing rate: S:slow, F:fast

Sample #	Fruit	Rank			
		First	Second	Third	Fourth
1	Cherries	NS .190	IS .180	IF .130	NF -.140
2	Honeydew	NS .300	IS .260	NF -.037	IF -.530
3	Cantaloupe I	IS .675	NS .023	NF -.274	IF -.406
4	Strawberries I	IS .380	NS .095	NF -.095	IF -.380
5	Cantaloupe	IS .492	NS -.224	IF -.268	-
6	Strawberries	IS .737	NS .161	IF -.211	NF -.687
7	Cantaloupe (rehydrated)*	IS .333	NS .122	IF 0	NF -.454
8	Pears	IS .678	NF -.060	NS -.206	IF -.412
9	Peaches	IS .969	IF -.001	NS -.233	NF -.726
10	Pineapple	IS .687	IF .172	NS .111	NF -.926
11	Pears	NF .618	IS .326	NS -.266	IF -.678
12	Apples	IS 1.03	IF .250	NF -.518	NS -.787

* Only three samples giving maximum range of +.85↔0↔(-.85)

Table 8

Summarized significant results for organoleptic tests of freeze dried fruits

Normal Solids/Slow Freezing NS
Normal Solids/Fast Freezing NF

Increased Solids/Slow Freezing IS
Increased Solids/Fast Freezing IF

Sample		Difference Test	Preference Test		Ranking Test
		Taste	Preference*	Significance	(preferred is firs
1	Cherries	NSD	NS/NF 8/14 NS/IS 8/14 IS/IF 10/14	NSD NSD NSD	NSD
2	Honeydew	NSD	IS/IF 13/15 NS/NF 11/15 IS/NS 8/15	1% NSD NSD	IS/IF 1% NS/IF 1%
3	Cantaloupe	NS/IS 1% IF/NF 5% IS/NF 5%	IS/IF 11/13 IS/NS 11/13 NS/NF 7/13	5% 5% NSD	IS/IF 1% IS/NF 1% IS/NS 5%
4	Strawberries	NSD	IS/IF 10/14 NS/NF 8/14 NS/IF 8/14	NSD NSD NSD	IS/IF 5%
5	Cantaloupe	IS/NS 5%	IS/NS 14/19 IS/IF 15/19	NSD 5%	IS/IF 1% IS/NS 1%
6	Strawberries	NF/IS 1% NF/IF 1% NS/IS 5%	IS/NF 10/12 IS/NF 10/12 NS/NF 9/12	5% 5% NSD	IS/NF 1% IS/IF 1% IS/NF 1% IS/NS 5% IF/NF 5%
7	Cantaloupe (rehydrated)	NSD	NS/NF 9/12 IS/NS 8/12 IS/IF 8/12	NSD NSD NSD	IS/NF 5%

Table 8 (continued)

		Difference Test		Preference Test			Ranking Test	
		Taste		Preference*		Significance	(preferred is first)	
8	Pears	IS/IF	5%	IS/NS	7/10	NSD	IS/IF	1%
				NS/NF	5/10	NSD	IS/NS	1%
				IS/IF	8/10	NSD	IS/NF	5%
9	Peaches	IS/NS	1%	IS/IF	11/12	1%	IS/IF	1%
		IS/NF	1%	NS/NF	9/12	NSD	IS/NS	1%
		IF/NF	1%	IS/NS	12/12	0.1%	IS/NF	1%
		IF/NS	5%				IF/NF	1%
		IS/IF	5%				NS/NF	5%
10	Pineapple	NF/NS	1%	IS/IF	8/12	NSD	IS/NS	1%
		NF/IF	1%	IS/NS	7/12	NSD	IS/NF	1%
		NF/IS	1%	IS/NF	11/12	1%	IF/NF	1%
		IS/NS	5%				NS/NF	1%
							IS/IF	5%
11	Pears	NF/IF	1%	NF/NS	8/10	NSD	NF/IF	1%
				IS/NS	8/10	NSD	NF/NS	1%
				IS/IF	9/10	5%	IS/IF	1%
							IS/NS	5%
12	Apples	IS/NF	1%	IS/IF	12/12	0.1%	IS/NS	1%
		IS/NS	1%	NF/NS	8/12	NSD	IS/IF	1%
		IF/NF	1%	IS/NS	12/12	0.1%	IS/NF	1%
		NS/IF	1%				IF/NS	1%
		IS/IF	1%				IF/NF	1%
							NS/NF	5%
13	Apples (rehydrated)	NS/IS	1%	IS/NS	13/13	0.1%	-	
		NS/IF	1%	IS/IF	12/13	1%		
		IS/IF	5%					

* Number of judges preferring a given treatment/total number of judges

Table 9

Summarized relative evaluation of quality

Sample #	Fruit	Preference tests	Ranking
1	Cherries	NS > NF,IS > IF	NSD
2	Honeydew	IS > NS $\overset{?}{>}$ IF > NF	NS,IS
3	Cantaloupe	IS > IF,NF,NS	IS
4	Strawberries	IS $\overset{?}{>}$ NS $\overset{?}{>}$ NF,IF	IS
5	Cantaloupe	IS > NS > IF	IS
6	Strawberries	IS > NS,IF > NF	IS
7	Cantaloupe (rehydrated)	IS > IF,NS > NF	IS
8	Pears	IS > NS,IF,NF	IS
9	Peaches	IS > NF > IF,NS	IS
10	Pineapple	IS,NS,IF > NF	IS
11	Pears	IS,NF > NS,IF	IS,NF
12	Apples	IS > NF,IF > NS	IS
13	Apples (rehydrated)	IS > IF,NS	-

6.1 Summary of Results

1) Techniques were developed which allow the identification and characterization of lipid phases in freeze dried oil-in-water emulsions.

2) The fraction of the oil that is present as inclusions is quite easily distinguished in the optical microscope, especially when techniques involving staining at highly refractive materials such as 1-bromonaphthalene are used.

3) Methods have been developed which permit viewing the same areas of a sample with the optical and scanning electron microscopes. The ability to compare observations by these two methods greatly improves the interpretation of features noted in either instrument.

4) It has been shown that oil which is not fully incorporated into the solid matrix can be extracted with organic solvents without disruption of the matrix, and is presumed to be present as surface deposits, either as free globules or a surface film.

5) Osmic acid has proved useful for identification of free fat in the optical microscope.

6) When humidified dry milk samples are heated at high temperatures, the extent of browning is related to sample particle size, due, most likely to differences in heat transfer.

7) Browning during the freeze drying of milk is influenced more by time of heating at high temperatures and

and low moisture than by heating at lower temperatures at higher moistures. This leads to a gradient of brown color through the thickness of a sample, with the highest browning at the free surface.

8) It was demonstrated that high rates of freeze drying could be achieved with little browning. If the samples were crushed to distribute any lightly browned surface material, they were virtually indistinguishable visually.

9) Decreasing sample thickness to 6 mm gave reduced drying times, but drying rates were similar to those of 12 mm samples. At the higher heating temperatures, the browning was significant, probably due to a larger proportion of surface.

10) Increasing the sample concentration resulted in sizable increases in drying rate and dry product output, but at a cost of increased browning. However, this method was preferable to improving drying rates by increasing heater temperatures.

11) The visual ranking of dry and rehydrated samples correlates well with browning values.

12) The solubility of dried milk powder correlated with extent of high temperature heating and browning value.

13) Visual organoleptic evaluations showed that surface geometry was important in determining effective powder color. In all studies, the freeze dried powders (including

some which were heated) were whiter than the original spray-dried powder (which had a yellow cast). In visual comparison tests, the spray dried powder was always judged unacceptable.

14) Levels of browning which were considered "acceptable" by the panel were twice as high when samples were judged independently than when viewed as a group.

15) Visual assessment of the browning of whole egg due to high temperature heating was best related to browning values measured on a chloroform or ether extract of the powder.

16) KCl extracts of the egg powder appear to measure colorless intermediates produced in the browning reaction and cannot be related to visual assessments of brown color.

17) It has proved difficult to develop an analytical test for browning value of fruits which correlates well with ranking based on visual evaluations. Visual evaluations do correlate well with times of heating at elevated temperatures.

18) Apple slices can be freeze dried at high temperatures without significant browning. The taste of the dried product was judged "different, but acceptable" and similar in quality to that of cooked apples. Sizable increases in product throughput were achieved by drying multiple layers of apple slices at elevated temperatures.

19) Osmotically treated fruit have been shown to be more sensitive to heating following freeze drying than to heating at the same temperature during the freeze drying process.

20) Computer simulations based on experimentally obtained data can be used to predict freeze drying behavior under various freeze drying conditions.

21) Sensory quality of the calcium alginate gels has been improved by the incorporation of pectin into the system.

22) A two step gelling procedure was developed, in which a thermal-gelling step is followed by a chemical gelling step. The procedure has shortened the required gelling time, and the handling and preparation has been simplified.

23) It has been found that major damage to the textural quality of the gel in freezing is probably due to the mechanical forces exerted by expanding ice crystals. Partial dehydration to remove 20-30% water content of the gel by either air drying or osmosis against a 50% sucrose solution prior to freezing has proved to be very effective to minimize this damage. Addition of microcrystalline Avicel to provide more nucleation sites hence resulting in a frozen sample with more, smaller ice crystals may also have contributed to the minimization of freezing damage.

24) Gels were developed which have after freeze-thawing a texture similar to that of fresh (unfrozen) gels.

25) It was found that the textural deterioration of the freeze dried and rehydrated gel occurred during the freeze drying procedure itself. The most disruptive factor was apparently the melting of the gel during the early stages of freeze drying. This has been significantly reduced or prevented by chilling the frozen samples in liquid nitrogen prior to insertion in the freeze dryer.

26) Application of the artificial food matrix in real food systems have been evaluated. When used as a fruit-piece substitute and incorporated into food systems such as jello, yogurt or cakes, the performance of the artificial food matrices is satisfactory, and acceptability is high.

27) Sucrose and maltodextrin have been utilized as osmotic agents for processing fruit slices prior to freeze drying. Osmotically treated samples were preferred over non-osmotic samples, with sucrose being slightly preferred as osmotic agent.

28) Two methods for contracting the fruits with the osmotic solutions (circulation and vacuum infusion) showed essentially no difference in product quality.

29) In general the preferred treatment for preparing high quality freeze dried fruit was an osmotic pretreatment with sucrose and slow freezing. Most pro-

ducts were rated as "good" or "very good" when evaluated in the dry or rehydrated state.

30) Studies of storage stability indicate that moisture uptake is the most important contribution to quality loss. Preliminary indications are that maintenance of highest product quality may also depend on protection against oxygen transport.